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**Annele Virtanen:** On the atmospheric implications of the solid phase and phase transitions of secondary organic aerosols

**Kyoko Tanaka:** Nucleation processes revealed by large-scale molecular dynamics simulations

**Robert McGraw:** Temperature dependence in heterogeneous and homogeneous nucleation

**Markku Kulmala** Legacy of SMEAR II observatory

**Thomas Peter** Heterogeneous versus homogeneous nucleation of ice in the upper troposphere and lower stratosphere

**Timo Vesala** 8-hours study of heat transfer in saunas over 21 years

**Lin Wang** Atmospheric nucleation in urban China
ON THE ATMOSPHERIC IMPLICATIONS OF THE SOLID PHASE AND PHASE TRANSITIONS OF SECONDARY ORGANIC AEROSOLS
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Keywords: secondary organic aerosol, physical phase, semisolid, diffusion limitations, viscosity

INTRODUCTION

Atmospheric secondary organic aerosols (SOA) result from gas-phase oxidation of volatile organic compounds (VOC), which are emitted from anthropogenic and biogenic sources. Chemical aging of the SOA particles in the atmosphere controls their physical and chemical properties such as phase state, volatility and hygroscopicity. All these factors can affect the particles’ ability to act as cloud condensation nuclei (CCN) and ice nuclei or to scatter and absorb solar radiation.

Several recent studies have shown that SOA particles can be in a semisolid physical phase depending on the particle composition and surrounding humidity conditions (Virtanen et al. 2010, Renbaum-Wolff et al. 2013, Pajunoma et al. 2015). The phase state of amorphous material is typically represented by the viscosity of the material: materials with viscosities less than 10^2 Pa s are considered liquids, with 10^2 – 10^12 Pa s as semisolids, and viscosities greater than 10^12 Pa s represent amorphous solid, glassy, material. Material’s viscosity depends on temperature and relative humidity as particle-phase water can act as a plasticizer and can decrease the viscosity of the material. The semisolid or solid phase state of the SOA particles may affect the atmospheric processes of the particles. The solid phase can limit the diffusion of condensable gas-phase molecules from the surface into the particle bulk and vice versa. This may affect inner mixing and disturb the equilibrium in gas/particle partitioning and result in slower evaporation of the particles than expected (Vaden et al. 2011, Yli-Juuti et al., 2016). The transport of small molecules (e.g. H_2O and oxidants) within the particle phase may also be affected by the diffusion limitations. This may in turn slower the chemical reactions in the organic matrix of SOA particles (Hinks et al., 2016; Marshall et al., 2016). In this presentation the relevance of the semisolid phase of the organic particles for the most central atmospheric aerosol processes is reviewed based on laboratory and atmospheric measurements of SOA particles.

METHODS

In this presentation I will discuss the physical phase of organic dominated aerosol particles both in atmospheric conditions and in laboratory experiments. For atmospheric observations I will review the recent literature as well as present our measurements performed using the aerosol bounce instrument (ABI, Pajunoma et al., 2015). The observations spans from monoterpene dominated boreal environments to isoprene dominated environments. Also the effect of atmospheric aging on physical phase and phase transitions is investigated.

For laboratory experiments I will discuss our studies on how the VOC precursors and O:C ratio of formed SOA affect the phase state of SOA at different humidity values. The main goal of our laboratory studies was to explore the possible effects of semisolid phase state of SOA particles on uptake of water or organic vapors. In one set of experiments the particles were generated by using flow tube reactors and the water uptake was investigated both at sub and supersaturation conditions using hygroscopic Tandem Differential Mobility Analyzer (HTDMA) and Cloud Condensation Nuclei counter (CCNc) respectively. In another set of experiments, the partitioning of organic vapors was investigated by measuring the evaporation rate of SOA particles using the setup presented in the figure 1. In the experiments both the single precursor VOCs...
as well as VOCs emitted by plants were used. In addition to these studies, recent literature results are reviewed.

Figure 1. Measurement setup to investigate the particle evaporation.

CONCLUSIONS

Several studies clearly show, that at dry conditions at room temperature, the diffusion limitations in semisolid SOA particle bulk play a role when the mixing of molecules in the particle bulk in atmospherically relevant time scales are considered (e.g. Vaden et al., 2011; Hinks et al., 2016; Liu et al., 2016; Yli-Juuti et al., 2017). When the humidity is increased to atmospherically relevant RH values, the picture gets more complicated as demonstrated in Figure 2 where the evaporation rate of a-pinene SOA particles at three different humidity conditions (RH~0%, 40% and 80%) are shown. As can be seen, the evaporation is clearly slower at dry condition compared to atmospherically relevant humidities (RH40% and 80%) indicating negligible effect of particle phase diffusion limitation to evaporation rate at atmospherically relevant RH values. This is due to the decreasing particle viscosity at elevated RH. Similar results are also reported by Ye et al. (2016) and Liu et al., (2016). Our field and laboratory studies also demonstrate, that the increasing O:C upon atmospheric aging further decreases the liquefying RH of atmospheric organic aerosols (Pajunoja et al., 2015 and 2016). The interpretation from our studies and studies by Ye et al and Liu et al. is that the particle diffusion is not rate-limiting to mass transfer of organic vapours in studied systems above 40% RH at temperatures close to room temperature. Our laboratory measurements also demonstrate that the dissolution of SOA particles from different precursors under subsaturation conditions is governed by the solubility characteristics of the particles rather than by diffusion limitations (Pajunoja et al., 2015).

By combining experimental evaporation rate results shown in Figure 2 with kinetic multilayer model, we can estimate both the volatilities of compounds in evaporating particles and particle viscosity changes during the evaporation at different humidities (see Fig. 2.). At dry conditions the viscosity of SOA particles increases up to values approx. $10^9$ Pas while at RH40% the values are order of magnitude lower. Also, of particular note is that considerable fraction (> 36%) of mass was needed in the two least volatile bins of the VBS ($C^* \leq 10^{-2}$ µg m$^{-3}$) to replicate the experimental results RH80%.
Most of the laboratory experiments on SOA physical phase presented in the literature are performed by very limited selection of precursor VOCs and at limited oxidation conditions. Also, the experimental investigations on diffusion limitation in SOA particle phase at lower temperatures are still completely lacking. Hence even if the experiments performed at room temperature indicate that diffusion limitations play only minor role in many atmospheric processes, the effect of lower temperatures on these processes is not known well enough. In addition, our recent laboratory studies indicate that the behavior of SOA particles generated using VOCs emitted by real plants may differ from the behavior of SOA from single precursors, such as a-pinene.

Figure 1. (A-B) Time evolution of particle size (diameter normalized with initial diameter). (C) Time evolution of the composition dependent particle viscosity. (D-F) Estimated initial particle dry composition if particles are liquid-like.

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REFERENCES


Marshall, F.H; Miles, R; Song, J; Ohm, P; Power, R; Reid, J; Dutcher, C. (2016) Diffusion and reactivity in ultraviscous aerosol and the correlation with particle viscosity Chem Sci, 2016, 7, 1298.


NUCLEATION PROCESSES REVEALED BY LARGE-SCALE MOLECULAR DYNAMICS SIMULATIONS

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Abstract

Although the homogeneous nucleation is a fundamental process, serious unreliability remains in model predictions for nucleation rates. We recently performed direct, large-scale molecular dynamics (MD) simulations of some homogeneous nucleation processes such as vapor-to-liquid nucleation and liquid-to-vapor nucleation. In the former case, $8 \times 10^9$ Lennard-Jones molecules (or $4 \times 10^6$ H$_2$O molecules) are used and the latter case calculates $5 \times 10^8$ Lennard-Jones molecules. These large system sizes allow us to measure extremely low and accurate nucleation rates. Our MD simulations of argon vapor-to-liquid nucleation succeeded in quantitatively reproducing the nucleation rates obtained in recent laboratory experiments at the same pressures and temperatures. We also measured other quantities such as the critical cluster size and the sticking probability. Large-scale MD simulations can also precisely determine the formation free energy of clusters over a wide range of cluster sizes owing to the good statistics on the cluster size distribution, which enables us to test the nucleation theory with a detail comparisons. Our results indicate that the classical nucleation theory needs updates in the surface energy of nano-sized clusters, the sticking probability, and the prefactor in the nucleation rate formula.

INTRODUCTION

The phase transition via homogeneous nucleation is a fundamental process and plays important roles in many areas of science and technology. Despite the familiarity of the process, serious unreliability remains in model predictions for nucleation rates. The classical nucleation theory (CNT) is a very widely used model for describing nucleation and provides the nucleation rates, however, several studies have found that the CNT fails to explain the nucleation rates observed in experiments. The deviations depend on the material, for instance, the rate predictions from the CNT disagree with measurements by factors of $10^{1-3}$ for water and $10^{10-20}$ for argon. In addition to laboratory experiments, numerical simulations of molecular dynamics (MD) or Monte Carlo (MC) simulations showed that the nucleation rates obtained by numerical simulations are significantly different from predictions by the CNT.

Molecular dynamics simulations are able to directly resolve details of the nucleation process and provide useful test cases for nucleation models. The size of the simulations such as the number of molecules and time-steps determines the nucleation rates that can be resolved. Typical MD simulations of homogeneous nucleation have used $10^5 - 10^6$ atoms. At low vapor densities, and therefore low supersaturations, a single nucleation event becomes unlikely to occur within reasonable computational timeframes. Large-scale simulations, however enable us to observe such rare nucleation events, and measure low nucleation rates. We recently performed direct, large molecular dynamics (MD) simulations of several homogeneous nucleation processes. In this paper, we introduce the results revealed by our MD simulations for three nucleation processes (vapor-to-liquid nucleation, crystallization in the droplets, and liquid-to-vapor nucleation). The simulations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code developed at Sandia National Laboratories and distributed as open source code which is a highly optimized, widely used, and well tested code.
VAPOR-TO-LIQUID NUCLEATION

(a) The case of Lennard-Jones molecule

Diemand et al. (2013) presented large-scale molecular dynamics (MD) simulations of homogeneous vapor-to-liquid nucleation of \((1 - 8) \times 10^9\) Lennard-Jones molecules, covering up to 1.2 \(\mu\)s (5.6 \(\times\) 10^7 steps). We used the Lennard-Jones potential

\[
u(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}, \tag{1}\]

with a cutoff at 5\(\sigma\). The simulation box has periodic boundary conditions. The time-steps are set to \(\Delta t = 0.01\tau = 0.01\sigma\sqrt{m/\epsilon}\). In the argon system the units are \(\epsilon/k = 119.8\) K, \(\sigma = 3.405\) Å, \(m = 6.634 \times 10^{-23}\) g and \(\tau = 2.16\) ps. The simulation runs cover a wide range of temperatures and supersaturation ratios, i.e., \(T^* = kT/\epsilon = 0.3 - 1.0\) and \(S = 1.5 - 1.5 \times 10^4\) where the supersaturation ratio \(S\) is defined by \(S = P_t/P_{sat}\) by using the saturated vapor pressure \(P_{sat}\) and the partial pressure of monomers \(P_1\).

Figure 1 illustrates the evolution of cluster counts and supersaturation ratio \(S\) for \(T^* = 0.8\) and a relatively high initial supersaturation ratio (left panel). The nucleation rate \(J\) is obtained from the slopes of least squares linear fits to \(N(> i)\) (Yasuoka and Matsumoto, 1998a; 1998b). As evident in Figure 1, the good statistics of this run allow us to measure the nucleation rate especially precisely. Figure 1 also shows the nucleation rates \(J\) obtained by our MD simulation runs for various temperatures and supersaturation ratios (the right panel). Most laboratory measurements of Argon nucleation probe nucleation rates lower than \(10^9\) cm\(^{-3}\) s\(^{-1}\) (e.g., Iland et al., 2007). The recent development of Laval Supersonic Nozzle (SSN) nucleation experiments (Sinha et al., 2010) has increased the accessible rates enormously, by almost 10 orders of magnitude. Together with the decrease in accessible \(J\) rates by over \(10^6\) reached in the MD simulations presented here, we have succeeded in direct comparisons of MD simulations with laboratory experiments at the almost same values of the parameters, \(T^*\) and \(S\). For the case of Argon, SSN experiments have been performed in the temperature range of 34 to 53 K and estimated nucleation rates of \(10^{17.1}\) cm\(^{-3}\) s\(^{-1}\) (Sinha et al., 2010). The temperature range overlaps with two of the values simulated here: \(T = 0.3\epsilon/k(= 35.94\) K\) and \(T = 0.4\epsilon/k(= 47.92\) K). Those two experimental data by (Sinha et al., 2010) are also plotted in Figure 1. We find very good agreement between the experiments and simulations within the uncertainties. As well as the nucleation rate, we also observed the sticking probabilities, temperatures, internal densities, and shapes of stable clusters (Angéll et al. 2014a).

The large-scale molecular dynamics simulations of homogeneous nucleation also allow us to accurately determine the formation free energy of clusters over a wide range of cluster sizes because large-scale simulations have a good statistics on the cluster size distribution. Tanaka et al. (2014b) presented a new method to obtain the free energies of cluster formation directly from MD results and compared them with predictions from three widely used models. The nucleation rate is the net number of the transition from \(i\)-mers to \(i + 1\)-mers and given by

\[
J = \left[ \sum_{i=1}^{\infty} \frac{1}{R^+(i) n_e(i)} \right]^{-1}, \tag{2}\]

where \(n_e(i)\) is the equilibrium size distribution. The accretion rate \(R^+(i)\) is the transition rate from a cluster of \(i\) molecules, \(i\)-mer, to \((i+1)\)-mer per unit time and given by \(R^+(i) = \alpha n(1)v_{ch}(4\pi r_i^2/2)!^{2/3})\), where \(\alpha\) is the sticking probability and \(v_{ch} = \sqrt{kT/2\pi m}\) is the thermal velocity.

The equilibrium size distribution is directly related to the formation free energy of a cluster as

\[
n_e(i) = n(1) \exp \left\{ \frac{\Delta G_i}{kT} \right\}, \tag{3}\]

where \(n(1)\) is the number density of the monomers (Wedekind et al., 2007; Tanaka et al., 2011; Diemand et al., 2013). Accordingly, the formation energies \(\Delta G_i\) govern the equilibrium size distribution and the nucleation rate. At the critical cluster size \(i^*\), \(\Delta G_i\) attains its maximum and \(n_e(i)\) is minimum.
There exists three models for the formation energies $\Delta G_i$, the classical nucleation theory (CNT), the modified classical nucleation theory (MCNT), and the semi-phenomenological (SP) model (Dillman and Meier, 1991; Laaksonen et al., 1994). In each model, the formation energy $\Delta G_i$ is given by

$$
\Delta G_{i,\text{CNT}} = -kT \ln S + 4\pi r_0^2 \gamma_0 i^{2/3},
$$

$$
\Delta G_{i,\text{MCNT}} = -(i-1)kT \ln S + 4\pi r_0^2 \gamma_0 (i^{2/3} - 1),
$$

$$
\Delta G_{i,\text{SP}} = -(i-1)kT \ln S + 4\pi r_0^2 \gamma_0 (i^{2/3} - 1) + \xi kT (i^{-1/3} - 1),
$$

respectively, where $\gamma_0$ is the surface tension of condensed phase. The monomer radius $r_0$ is given by $(3\pi n_0/4\pi)^{1/3}$, where $v_0$ is the volume per molecule of the condensed phase. The coefficient $\xi$ is determined so that the formation energy of a dimer $\Delta G(i=2)$ is consistent with the second virial coefficient. Although the CNT has a problem that $\Delta G(i=1)$ does not vanish, it is fixed in the MCNT. At a steady-state nucleation phase, the size distribution $n(i)$ deviates from the equilibrium value $n_e(i)$ for $i \gtrsim i^*$, though they agree well each other for $i \lesssim i^*$. However, we can evaluate $n_e(i)$ from $n(i)$ using the recurrence relation given by

$$
n_e(i) = \frac{n_e(i-1)}{n(i-1)} \left( 1 - \frac{J}{R^*(i-1)n(i-1)} \right)^{-1}.
$$

Fig. 2 shows $n_e(i)$ and $\Delta G_i(S)$ derived from Eqs. (3) and (7) for a typical example ($T^* = 0.6$ and $S = 16.9$). The left of Figure 2 shows $\Delta G_i(S = 1)$, which corresponds to the second term (or the surface term) of the formation energy (see Eqs. (4)-(6)). At all temperatures, the MD results agree well with the SP model for relatively small clusters.

We also find that the ratio of $\Delta G_i(S = 1)$ to the CNT value, $4\pi r_0^2 \gamma_0 i^{2/3}$, is almost independent of temperature for $T^* \leq 0.8$. For this temperature range, we obtain a fitting formula as

$$
\frac{\Delta G_i(S = 1)}{4\pi r_0^2 \gamma_0 i^{2/3}} = 1.28(1 - i^{-1/3}).
$$

The fitting formula is useful for large clusters with $i \gtrsim 10$, where the prediction by the SP model is inaccurate. For sufficiently large clusters, the surface term is expected to approach to the CNT value (i.e., the ratio should become unity). However, our MD simulations do not show such tendency even for $i \sim 100$. Much larger simulations seem to be required to observe the
Figure 2: (a) The formation free energy $\Delta G_i(S)$ as a function of $i$ for the case of $T^* = 0.6$ and $S = 16.9$. The dashed line shows $\Delta G_i(S = 1) = \Delta G_i(S) + (i - 1)kT\ln S$. (b) The equilibrium number density of $i$-mers $n_i(0)$ (solid curve) and the steady number density $n_i(t)$ (dots) in unit of $\sigma^{-3}$. (c) The surface term $\Delta G_i(S = 1)$ as a function of $i^{-1/3}$ for $T^* \leq 0.6$ (d) and for all temperature (e). The MD results are plotted by triangles or circles. Dotted lines represent the SP model. Thick and thin lines show the CNT and MCNT, respectively. From Tanaka et al. (2014b).

The case of water

We also performed direct large-scale molecular dynamics simulations of water droplet nucleation, using up to $4 \times 10^6$ SPC/E H$_2$O molecules (Angélil et al., 2015). The SPC/E is a widely-used, rigid 3-site H$_2$O model, which registers Coulombic interactions, as well as polarization corrections to each site, and further adds a Lennard-Jones component to the oxygen atom potential (Berendsen et al., 1987). Our large system sizes allow us to measure extremely low and accurate nucleation rates, down to $10^{10}$ cm$^{-3}$s$^{-1}$, helping close the gap between experimentally measured rates $10^{13}$ cm$^{-3}$s$^{-1}$. Comparison to nucleation models shows that the classical nucleation theory over-estimates nucleation rates by a few orders of magnitude. The SP model does better, under-predicting rates by at worst a factor of 24. The sticking probabilities $\alpha$ lie in a range of $0.06 - 1.3$ in our MD simulations (Tanaka et al., 2014a; Angélil et al., 2015) and they have a trend of decreasing $\alpha$ with lower $S$, which is similar to the case of LJ system (Tanaka et al., 2011; Diemand et al., 2013).

We also re-calibrated a Hale-type $J$ vs. $S$ scaling relation (Hale, 1992; Hale, 2004; Hale, 2005; Hale and Thomason, 2010) using both experimental and simulation data for the case of water, Hale (2005) suggested that the nucleation rate was scaled by $\ln S/(T_e/T - 1)^{-1.5}$ for the experimental results of water over a range of $J = (10^4 - 10^{10})$ cm$^{-3}$s$^{-1}$. Tanaka et al. (2014b) showed that this scaling relation works well for large scale Lennard-Jones simulations and Argon laboratory experiments, albeit with an exponent of 1.3 instead of 1.5. We confirmed that same scaling relation applies well to our SPC/E water nucleation rate measurements (Fig.3). However, we find that the combined nucleation rates from both SPC/E simulations and laboratory experiments with water are even better scaled by $\ln S/(T_e/T - 1)^{1.7}$. The results from the MD simulations join smoothly with the experiments with the scaling. This empirical scaling relation seems to work well over a surprisingly wide nucleation rate range from $J = 10^{-2}$ to $10^{26}$ cm$^{-3}$s$^{-1}$ and 180 K in the temperature range for both MD simulations and experiments. This scaling relation also works very well for the SP model.

DROPLET CRYSTALLIZATION

It is often observed that droplets formed from vapor are supercooled liquids in nature and experiments, although crystallization is expected to occur at temperature below the triple temperature. This phenomenon is known as an example of Ostwald’s step rule in which a metastable phase appears first before a stable phase. In Diemand et al. (2013), the nuclei of liquid appear even the lower temperature than the triple point and the crystallization in them was observed only rarely. We performed MD simulations of homogeneous vapor-to-solid phase transition of
Lennard-Jones molecules, which shows multistep nucleations of formation of liquid-like particles (first step nucleation) and crystallization in those (second step nucleation). During a long direct NVE (constant number of molecules, volume and energy) integration up to 200 million steps (= 4.3 µs), the nuclei of supercooled liquid appear and growth. Crystal structure is identified using the Common Neighbor Analysis (CNA) method (Faken and Jónsson, 1994; Tsuzuki et al., 2007) implemented in LAMMPS. The crystallizations of many large supercooled nano-clusters are observed after the liquid particles growth to a size (~ 800 molecules at $T \simeq 0.5\varepsilon/k$). Some of them crystallize quickly and almost completely. We found all crystallized clusters lose a few % of their mass at freezing and every mass loss of this kind is associated with crystallization. The mass loss is caused by evaporation, since the latent heat from freezing heats up the cluster.

The crystallized clusters composed of ~ (1000 – 5000) atoms show various structures in our simulations. Figure 4 shows the projections of atomic positions in several crystallized clusters ~ 4000. Each has a characteristic structure for nano-particles, i.e., isosahedral (Ih), decahedral (Dh), face-centered cubic (fcc), and hexagonal close-packed (hcp). These several kinds of clusters are present in the same size range. In the simulations, once a liquid-like particle freezes, the crystal structure was kept during the growth of the crystal with the size up to 5000 molecules. Our results imply that the solid-solid transition does not occurs easily because of the energy barrier between different structures.

LIQUID-TO-VAPOR NUCLEATION

Next we present results from large-scale MD simulations of homogeneous bubble (liquid-to-vapor) nucleation in which the simulations contain half a billion Lennard-Jones molecules and
cover up to 56 million time steps (Diemand et al., 2014; Angéll et al., 2014b). In these simulations, the cut-off length of the LJ potential is set to be 2.5 $\sigma$. This large size of the simulated volumes allows us to resolve the nucleation and growth of many bubbles per run in simple direct micro-canonical simulations with almost constant pressure and temperature. The obtained bubble nucleation rates are lower than in most of the previous, smaller simulations. It is widely believed that classical nucleation theory (CNT) generally underestimates bubble nucleation rates by very large factors. However, our measured rates are within two orders of magnitude of CNT predictions; only at very low temperatures does CNT underestimate the nucleation rate significantly (Fig. 5).

To understand the deviation from the CNT prediction, we revisited classical nucleation theory (CNT) for the homogeneous bubble nucleation rate and improve the classical formula using a correct prefactor and a curvature-dependent surface energy in the nucleation rate. The bubble nucleation rate is the number of stable bubbles formed per unit time per unit volume and is given by (Blander and Katz, 1975)

$$J = J_0 n_b(i_c), \tag{9}$$

where $i_c$ is the number of vapor molecule in a critical bubble, $J_0$ is the prefactor in the nucleation rate, and $n_b(i)$ is the number density of bubbles. In the previous theoretical studies, an oversimplified constant prefactor has often been used, which is determined by the bubble growth rate due to the evaporation at liquid surface of bubbles. However, the growth of bubbles is also regulated by the thermal conduction, the viscosity, and the inertia of liquid motion (Kagan, 1960). These effects can decrease the prefactor significantly, especially when the liquid pressure is negative. The deviation in the nucleation rate between the improved formula and the CNT can be as large as several orders of magnitude (Fig. 6, left panel). We newly presented the explicit form of the accurate prefactor $J_0$ (Tanaka et al. 2015). Our improved, accurate prefactor enables us to precisely constrain the free energy barrier for bubble nucleation at the comparisons of theories with recent MD simulations and laboratory experiments for argon bubble nucleation.

The surface energy is generally dependent on the curvature of the surface and, in the Helfrich expansion, it is given by

$$\gamma = \gamma_0 + \frac{2\delta \gamma_0}{r} + \frac{2k + \hat{k}}{r^2}, \tag{10}$$

where $r$ is the radius of curvature, and $\delta \gamma$, $k$, and $\hat{k}$ are coefficients (for detail, see Helfrich, 1973; Wilhelmsen et al., 2015). Wilhelmsen et al. (2015) calculated the values of $\gamma_0$ and these coefficients for LJ system with various cut-off lengths including 2.5 $\sigma$. In the double sign of Eq. (10), the upper one (i.e., +) corresponds to the bubble case while the lower is the droplet case. Hence this reasonable expression should be used at comparisons with MD simulations (Schmelzer and Baidakov, 2016). Figure 6 (right panel) shows comparisons in the surface tension between Helfrich’s model [Eq. (10)] and the estimated values from MD simulations (Tanaka et al., 2016). In Helfrich’s model, we used the coefficients with the cut-off length of 2.5 $\sigma$ obtained by Wilhelmsen et al. (2015).

Figure 6 shows that the model of Eq. (10) well reproduces all the results of our MD simulations with relatively large critical bubble size ($> 2\sigma$). It should be noted that Eq. (10) might be inaccurate for very small bubbles. Sufficiently small bubbles also require higher order terms than the second order in the Helfrich expansion. Wilhelmsen et al. (2015) pointed out that Eq. (10) is valid only when $\gamma/\gamma_0 \lesssim 0.8$ at $T^* = 0.9$. Baidakov and Bobrov (2014) estimated the surface tension of bubbles smaller than 2 $\sigma$ from their MD simulations and found deviations from Eq. (10) with reasonable coefficients. Further investigation on the valid range of Eq. (10) should be done in future work.

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Figure 5: Measured nucleation rates divided by the classical nucleation theory including Poynting correction (PCNT) estimate against $T/T_c$ for our simulations (green diamonds) and bubble nucleation results from the literature. From Diemand et al. (2014).

Figure 6: (Left) The prefactor obtained by Eq. (49) of Tanaka et al. (2015) as a function of the liquid pressure $P_l$. From Tanaka et al. (2015). (Right) Surface tensions at $T^* = 0.6, 0.7, 0.8$ and 0.855 (open symbols). Solid lines show Eq. (10). From Tanaka et al. (2016).

REFERENCES


TEMPERATURE DEPENDENCE IN HOMOGENEOUS AND HETEROGENEOUS NUCLEATION

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INTRODUCTION

Heterogeneous nucleation on stable (sub-2 nm) nuclei aids the formation of atmospheric cloud condensation nuclei (CCN) by circumventing or reducing vapor pressure barriers that would otherwise limit condensation and new particle growth. Aerosol and cloud formation depend largely on the interaction between a condensing liquid and the nucleating site. A new paper published this year reports the first direct experimental determination of contact angles as well as contact line curvature and other geometric properties of a spherical cap nucleus at nanometer scale using measurements from the Vienna Size Analyzing Nucleus Counter (SANC) (Winkler et al., 2016). For water nucleating heterogeneously on silver oxide nanoparticles we find contact angles around 15 degrees compared to around 90 degrees for the macroscopically measured equilibrium angle for water on bulk silver. The small microscopic contact angles can be attributed via the generalized Young equation to a negative line tension that becomes increasingly dominant with increasing curvature of the contact line. These results enable a consistent theoretical description of heterogeneous nucleation and provide firm insight to the wetting of nanosized objects.

A second paper (McGraw et al. submitted) uses the direct experimental determination approach to examine temperature dependence of heterogeneous nucleation. As in Winkler et al. (2016), which focused on the isothermal case, we again use measurements from the SANC but for fixed seed diameter and over a temperature range (Kupc et al., 2013). Our re-examination of the Kupc et al. measurements uses, first, a model-free theoretic framework, based on the second nucleation theorem (McGraw et al., submitted). The analysis, summarized below, provides a determination of the energy of critical cluster formation directly from the SANC measurements of nucleation probability (c.f. Fig. 1). Temperature dependence is correlated quantitatively through the measurements with stabilization of the water cluster by the silver oxide nanoparticle seed and the findings are used to interpret the unusual temperature dependence found by Kupc et al. (2013) for this system. A necessary condition found here for the observed unusual positive temperature dependence (increasing $S_{\text{onset}}$ with increasing temperature $T$ where $S_{\text{onset}}$ is the onset value of the water vapor saturation ratio defined more precisely below) is that the critical cluster be more stable on a per molecule basis than the bulk liquid; i.e., the energy lowering through stabilizing molecular interactions between cluster and seed has to more than compensate the positive contribution from surface energy in order to exhibit the effect.

TEMPERATURE DEPENDENCE VIA THE SECOND NUCLEATION THEOREM

The first and second nucleation theorems provide direct microscopic information about the nucleation processes at near molecular scale. Of these the first theorem, which determines molecular number content of the critical nucleus from dependence of the nucleation rate on saturation ratio, is the more commonly used. While both are vital to the analysis, the second nucleation theorem, which infers critical cluster energy from dependence of nucleation rate on temperature (Ford, 1997; McGraw and Wu, 2003), is
central to the present study. For the homogeneous nucleation case where \( g^* \) molecules of vapor \( A_j \) combine to form a critical size cluster \( A_{g^*} \):

\[
\left( \frac{\partial \ln J_{\text{hom}}}{\partial T} \right)_S = \frac{E_{A_{g^*}} - g^* E_{A_{g^*}}^\text{bulk}}{kT^2} + \frac{E_{A_{g^*}} - E_{A_{g^*}}^\text{bulk}}{kT^2}.
\] (1)

Here \( E_{A_{g^*}} \) is the energy of forming the critical cluster relative to the energy in \( g^* \) molecules of bulk liquid each molecule having energy \( E_{A_{g^*}}^\text{bulk} \), \( J_{\text{hom}} \) is the homogeneous nucleation rate per unit volume, \( S \) is the vapor saturation ratio and \( k \) is the Boltzmann constant. The second term on the right hand side is the energy required to vaporize a single molecule from bulk liquid that emerges from the analysis used to derive Eq. 1 (Ford, 1997).

It is interesting that the bulk liquid reference state enters into consideration of molecular cluster formation from vapor. As shown below this is due to holding \( S = n_1 / n_1^{\text{eq}} \) constant in the partial derivative, where \( n_1 \) is the vapor number concentration and \( n_1^{\text{eq}} \) its value in equilibrium with bulk liquid. Holding, instead, \( n_1 \) constant gives a different result:

\[
\left( \frac{\partial \ln J_{\text{hom}}}{\partial T} \right)_{n_1} = \frac{E_{A_{g^*}} - g^* E_{A_{g^*}}}{kT^2},
\] (2)

in which the bulk reference state no longer appears. Equations 1 and 2 explain the temperature dependences seen in homogeneous nucleation studies as follows: On a per molecule basis the energies of either the cluster or the vapor exceed the energy of the bulk liquid with the result that the right hand side of Eq. 1 is always positive. Similarly, the energy of the cluster, again on a per-molecule basis, is less than that of the vapor implying that the right hand side of Eq. 2 is always negative. This results in the following inequalities for temperature dependence of the nucleation rate:

\[
\left( \frac{\partial \ln J_{\text{hom}}}{\partial T} \right)_s > 0 \quad \text{(3a)}
\]

\[
\left( \frac{\partial \ln J_{\text{hom}}}{\partial T} \right)_{n_1} < 0 , \quad \text{(3b)}
\]

which are in agreement with measurement.

Consider next the heterogeneous nucleation case described at the molecular level by the association reaction:

\[
M + n^* A_j \Leftrightarrow MA_{n^*}
\] (4)

where \( M \) is a single seed particle and \( MA_{n^*} \) is the critical cluster complex. The use of \( n^* \) here is to distinguish from the homogeneous case. The analogs to Eqs. 1 and 2 for the heterogeneous case are:

\[
\left( \frac{\partial \ln J_1}{\partial T} \right)_s = \frac{E_{MA_{n^*}} - n^* E_{A_j}^\text{bulk} + E_{A_j} - E_{A_j}^\text{bulk}}{kT^2}
\] (5a)

and
respectively. The right hand side of Eq. 5b is always negative, on account that the energy of the associated complex is always less than the sum of energies of the unassociated seed and completely dissociated vapor. For this case, holding \( n_1 \) constant in the partial derivative,

\[
\left( \frac{\partial \ln J_1}{\partial T} \right)_{n_1} < 0
\]  

(6a)

and the inequalities for the homogeneous and heterogeneous nucleation cases have the same sign. Equation 5a is more interesting in that the lead term on the right hand side, and thus the whole right hand side, can have either sign:

\[
\left( \frac{\partial \ln J_1}{\partial T} \right)_{S} > 0
\]  

(6b)

The reason for the ambiguity is that the lead numerator in Eq. 5a reflects the difference in energy between the critical cluster-seed complex and the sum of energies for a free seed particle and \( n^* \) molecules of bulk liquid. Sufficiently attractive seed-cluster interactions can overcome the positive surface energy at the cluster-vapor interface so as to make the leading term on the right hand side of Eq. 5a negative, which is the necessary condition for the entire right hand side to be negative, resulting in the unusual (for \( S \) held constant in the partial derivative) temperature dependence given by the lower (less than) inequality of Eq. 6b. Sufficiency requires sufficiently attractive seed-cluster interactions to overcome both the cluster surface energy and the vaporization terms that the entire right hand side of Eq. 5a is negative. Otherwise the upper (greater than) inequality of Eq. 6b is maintained and the temperature dependencies are of the same “usual” sign in both the homogeneous and heterogeneous nucleation cases, irrespective of whether the saturation ratio or the number concentration of molecules in the vapor is held constant in the partial derivative.

ANALYSIS OF MEASUREMENTS

The preceding section examined the sensitivity of nucleation rate with respect to temperature and its sign. However, the SANC measurements, (Kupc et al., 2013) and (Schobesberger et al., 2010), don’t measure nucleation rate directly but instead measure nucleation probability, as shown for a typical measurement set in Fig. 1. These measurements allow one to determine both the onset saturation ratio, \( S_{onset} \), defined such that \( P(S_{onset}) = 1/2 \), and \( n^* \), which is related to the slope \( (dP / dS)_{S=S_{onset}} \) evaluated at \( S_{onset} \). The connection between the per-unactivated-seed nucleation rate, \( J_1(S) \) of the previous section (units \( s^{-1} \)), and \( P(S) \) can be written (McGraw et al., 2012):

\[
P(S) = 1 - \frac{N(t_{res})}{N(0)} = 1 - e^{-J_1(S)t_{res}}
\]  

(7)

where \( N(t_{res}) \) is the concentration of unactivated particles at the residence time \( t_{res} \), defined by the operating conditions of the SANC, and \( N(0) \) is the initial seed concentration. From these considerations it follows from Eq. 7 that \( J_1(S_{onset})t_{res} = \ln(2) \), which result is used to eliminate the residence time, \( t_{res} \). A convenient expression for \( P(S) \), the Gumbel distribution (Gumbel, 1958), derives naturally from the first nucleation theorem applied to the per-seed nucleation rate. The result, which requires no specific model of
the nucleation process, only the fundamental laws of mass action and detailed balance on which the first nucleation theorem itself is based, is the inverse of an equation obtained by Vehkamäki et al (2007) for \( n^* \) in terms \( P(S) \):

\[
P(S) = 1 - \exp \left\{ -\exp \left[ \ln(2) + \left( n^* + 1 \right) \left( \ln S - \ln S_{\text{onset}} \right) \right] \right\}.
\]  

(8)

Here \( n^* \) follows Eq. 8 as the slope of \( P(S) \) evaluated at \( S_{\text{onset}} \):

\[
\left( \frac{dP}{dS} \right)_{S = S_{\text{onset}}} = \frac{(n^* + 1) \ln 2}{2S_{\text{onset}}}
\]

(9)

Figure 1: Nucleation probability vs. \( S \) for heterogeneous nucleation of water on AgO nanoparticles at 278K. Geometric seed particle diameter = 3.2 nm. Data points, measurements form the Size Analyzing Nucleus Counter (SANC). Dashed line gives the nucleation onset condition \( P(S_{\text{onset}}) = 0.5 \). Curve, Gumbel distribution (Eq. 8) in terms of the two measured parameters \( S_{\text{onset}} \) and \( n^* \) where \( n^* \) is the number of water molecules present in the critical seed-cluster complex. Adapted from Winkler et al., 2016.

To make contact with the nucleation probability curves, we examine how \( S_{\text{onset}} \), indicated by the point of intersection of the dashed and solid curves in Fig. 1, varies with temperature. The \( S_{\text{onset}} \) condition maintains a constant per particle nucleation rate. At constant \( J_1 = J_1(S_{\text{onset}}) = \ln(2) / t_{\text{exp}} \):

\[
d \ln J_1 = \left( \frac{\partial \ln J_1}{\partial T} \right)_{S_{\text{onset}}} dT + \left( \frac{\partial \ln J_1}{\partial \ln S} \right)_T d \ln S = 0
\]

and rearrangement of the second equality gives:

\[
\left( \frac{\partial \ln S}{\partial T} \right)_{S_{\text{onset}}} = -\left( \frac{\partial \ln J_1}{\partial T} \right)_{S_{\text{onset}}} / \left( \frac{\partial \ln J_1}{\partial \ln S} \right)_T
\]

(10)

The numerator on the right is given by Eq. 5a and the denominator is given in terms of \( n^* \) by the first nucleation theorem:

\[
\left( \frac{\partial \ln J_1}{\partial \ln S} \right)_T = n^* + 1.
\]

(12)
Combining the first and second nucleation theorems from Eqs. 12 and 5a, respectively, with the chain rule, Eq. 11, gives the result we have been seeking (McGraw et al., submitted):

$$\left(\frac{\partial \ln S_{\text{onset}}}{\partial T}\right)_{T_1} = -\frac{(E_{\text{Mac}} - n^* E_{\text{bulk}} - E_M) + (E_A - E_{\text{bulk}})}{(n^*+1)kT^2} \tag{13}$$

The measurements of Kupc et al. (2013) show both usual and unusual behavior with a maximum in $S_{\text{onset}}$ occurring near 278K as seen in Table 1. This table lists the model-free parameters that can be obtained directly using the methods described in the previous section: $n^*$ follows from Eq. 9 and a parabolic fit to the three measurement points $\{T, \ln S_{\text{onset}}\}$ was used to generate estimates for the temperature derivative shown in column 5. These derivatives fix the left hand side of Eq. 13 and are used there together with $n^*$ and the known energy of vaporization from bulk liquid to obtain the energies of formation $\Delta E^{\text{hetero}}_f = E_{\text{Mac}} - n^* E_{\text{bulk}} - E_M$ shown in column 6.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$S_{\text{onset}}$</th>
<th>$\ln S_{\text{onset}}$</th>
<th>$n^*$</th>
<th>$d \ln S_{\text{onset}} / dT$</th>
<th>$\Delta E^{\text{hetero}}_f$ ($10^{-20}$ joule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>274</td>
<td>1.59</td>
<td>0.464</td>
<td>9.7</td>
<td>0.0423</td>
<td>-54.0</td>
</tr>
<tr>
<td>278</td>
<td>1.77±0.014</td>
<td>0.571</td>
<td>12.8±0.7</td>
<td>0.0112</td>
<td>-23.6</td>
</tr>
<tr>
<td>287</td>
<td>1.43</td>
<td>0.358</td>
<td>12.3</td>
<td>-0.0586</td>
<td>81.6</td>
</tr>
</tbody>
</table>

Table 1. Model-independent parameters $S_{\text{onset}}$ and $n^*$ are from fits to the experimental data by Eq. 8. The seed particle size is constant over the set of measurements at geometric radius $r_p (\text{nm}) = 3.35$, about twice as large as the seed particles used in the experiment recorded in Fig. 1. Unusual (positive) values of the temperature derivative are seen at lower temperatures followed by transition to normal dependence at higher temperature as indicated by the negative temperature derivative at 287K.

![Figure 2. Depiction of critical cluster energies per molecule for homogeneous and heterogeneous nucleation. The positioning of these energies relative to the bulk liquid and vapor reference states determines sign of the temperature dependence.](image-url)
Figure 2 depicts the disposition of critical cluster energy scales as determined from the present analysis. In homogeneous nucleation, the critical cluster, represented here by the unsupported cluster, always lies intermediate in energy between the vapor and bulk liquid reference states and sign of the temperature dependence (Eqs. 3a and 3b) is unambiguous. For the heterogeneous nucleation case, with special reference to the entries in Table 1, the temperature dependence can have either sign. For clusters lying intermediate in energy between the reference states the sign is normal, i.e. consistent with the homogeneous nucleation case (Eq. 6a) and the upper (greater than) inequality of Eq. 6b, as seen at the higher temperature 287K. At lower temperatures, stabilization of the critical cluster by the seed particle lowers the per-molecule energy below the bulk reference state value, which is the necessary condition for reversal of the sign of the temperature dependence (lower inequality of Eq. 6b) and an increasing $S_{net}$ with increasing temperature. This unusual temperature dependence occurs in the lower temperature range between 274 and 278K for the series of experiments described in connection with Table 1.

**TEMPERATURE DEPENDENCE IN THE FLETCHER MODEL**

The model-independent analysis of the preceding section, despite its generality, is somewhat abstract. For this reason it is useful to interpret the general results within the framework of Fletcher's classical spherical cap model of the critical cluster in heterogeneous nucleation (Fletcher, 1958). The analysis methods of Winkler et al., 2016, applied to the nucleation probability measurements, enable the direct determination of a unique microscopic contact angle from measured values of $S_{crit}$ and $n^*$. First, the cap radius of curvature at the liquid-vapor interface, $r^*$, is determined from $S_{crit}$ and the molecular volume and surface tension of water by the Kelvin relation:

$$r^* = \frac{2\gamma_0 \sigma_h}{kT \ln S_{crit}}$$  \hspace{1cm} (14)

Then from $r^*$, $n^*$, and the seed particle radius, $r_p$, the contact angle $\theta$, which is the key parameter for characterizing seed-cap interactions in the Fletcher model, is uniquely determined (Winkler et al., 2016). Additional microscopic parameters including area of the seed-cap interface $\Omega$, the polar angle $\phi$, and geodesic curvature of the three-phase contact line (Fig. 3) are also directly determined for use with the spherical cap model (Winkler et al., 2016). Numerical values computed for some of these quantities are given in Table 2. To-scale cross sections of the critical seed-cap assembly are shown in Fig. 4.

![Spherical cap model and notation used in the Fletcher theory. Disposition of the line tension force (not included in the Fletcher model) is also shown.](image)
Table 2. Continuation of Table 1 to include additional parameters derived using the Fletcher model. The critical radius, \( r^* \), results from the measured \( S_{\text{near}} \) via Eq. 14 using surface tension and density of water from Wölk and Strey (2001). \( \theta \) is the directly determined microscopic contact angle and \( d \cos \theta /dT \) its temperature dependence. \( \Omega_{sl} \) is the seed-cap contact area and \( \Delta H_w \) is the microscopic heat of wetting (Harkins and Jura, 1944; Neumann, 1974). The necessary condition for unusual temperature dependence in the Fletcher model is that \( d \cos \theta /dT < 0 \), which is satisfied (column 5) over the lower range of temperature as required for consistency with the energy criterion \( \Delta E_f^{\text{hetero}} < 0 \) (Table 1).

![Figure 4](image_url)

Figure 4. To-scale cross sections of the critical seed-cap assembly constructed using the parameters listed in Table 2 (scale is in angstrom units).

A physical interpretation for the energies derived from the second nucleation theorem analysis is again best achieved using a microphysical model. McGraw et al. (submitted) employ the classical heterogeneous nucleation model of Fletcher for this purpose (Fletcher, 1958). A key step in our calculation of cluster formation energies relative to the bulk liquid looks at the surface work and computes energies through the imaginary process of reversibly extending the adsorbed critical cluster from bulk liquid phase following the thermodynamic analysis for droplet extrusion introduced by Reiss (1965). The key interaction parameter in the Fletcher model is the contact angle \( \theta \), specifically \( \cos(\theta) \). For computing surface energies (rather than free energies) one requires additionally the temperature derivatives for both the liquid-vapor surface tension and \( \theta \), specifically \( d \cos(\theta)/dT \). As with the cluster formation energies, these are obtained from the dependence of \( S_{\text{near}} \) on \( T \) estimated from the measurements (entries in column 5 of Table 1).

Details of the calculations, only summarized here, are given in McGraw et al. (submitted).

A key finding from that work is that the necessary condition for unusual temperature dependence, formulated in the previous sections in terms of seed-cluster interaction energy, has a nice counterpart in terms of the contact angle in the Fletcher theory, namely: \( d \cos \theta /dT < 0 \), equivalently \( d\theta /dT > 0 \).

This condition, now firmly established theoretically, is consistent with the observation of Schobesberger et al. (2010) of being able to fit the Fletcher model to the unusual temperature dependence that they observed.
for n-propanol condensation on NaCl seed particles only by having the contact angle increase with increasing temperature.

ACKNOWLEDGEMENTS

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REFERENCES

Gumbel, E. J. (1958), Statistics of Extremes (Dover, Mineola, New York) pg. 159.
Reiss, H. (1965), Methods of Thermodynamics (Dover, Mineola, New York) Chap XI.
INTRODUCTION

The atmosphere forms a major part of the environment to which life on Earth is sensitively responsive. The atmosphere closely interacts with the biosphere, hydrosphere, cryosphere and lithosphere as well as with urban surfaces on time scales from seconds to millennia (Wanner et al. 2008). Changes in one of these components are directly or indirectly communicated to the others via intricately-linked processes and feedbacks resulting in local, regional and global scale effects on climate and air quality. In recent years, substantial research has been motivated by the importance of atmospheric aerosols on the global radiation budget, cloud formation, and human health (IPCC 2013, Rosenfeld et al. 2014, Apte et al. 2015, Lelieveld et al. 2015). Concentrations of reactive gases, greenhouse gases and atmospheric aerosol particles are tightly connected with each other via physical, chemical and biological processes occurring in the atmosphere, biosphere and at their interface (e.g. Arneth et al. 2010, Kulmala et al. 2014a). Human and societal actions, such as emissions-control policies, urbanization, forest management and land-use change, as well as various natural feedback mechanisms involving the biosphere and atmosphere, have substantial impacts on the complicated couplings between atmospheric aerosols, trace gases, greenhouse gases, air quality and climate (Shindell et al. 2012, Kulmala et al. 2015, Kulmala 2015).

In order to obtain the needed new knowledge, we need to perform i) targeted laboratory experiments, ii) continuous and comprehensive in situ observations in different types of environments or ecosystems and platforms, together with targeted gap-filling laboratory experiments, iii) ground- and satellite-based remote sensing, and iv) multi-scale modelling.

The backbone of our approach is continuous, comprehensive observations. The first and longest continuous comprehensive atmospheric and ecosystem data set is from SMEAR (Station for Measuring Ecosystem-Atmosphere Relations) II (Hari and Kulmala, 2005) located in Hyytiälä, Finland. The long and continuous data series along with versatile measurement equipment of the SMEAR II station provide continuous information on long-term trends in the aerosols, trace gases and greenhouse gases over boreal forests, combined with information on material and energy flows within the forest-atmosphere continuum, making it possible to test novel theories and instrumental techniques under boreal forest conditions. Being the leading observatory on its own field, the SMEAR II station has influenced (and has already its legacy) several different fields related to scientific research, research infrastructures and knowledge transfer.

SMEAR CONCEPT

The SMEAR concept has provided a valuable platform for conducting multi-disciplinary research on atmosphere-ecosystem exchange processes since 1995 when the SMEAR II station was established. Over that period, a network of SMEAR stations (Hari et al. 2016) was created, and the latest member of this station family became operable in Estonia during 2013. Together with the SMEAR I–IV stations (https://www.atm.helsinki.fi/SMEAR/) in Finland, the station transect spans more than 1000 km over the northern Europe. The stations are located in different parts of the boreal biome ranging from the subarctic...
to the hemi-boreal transition zone at the southern edge of boreal ecosystems. This feature makes it possible to investigate and compare processes over different climatic zones and different boreal ecosystems.

The SMEAR concept enables research on all kind of interactions in the atmosphere-Earth surface continuum. This surface can be a forest, wetland, river, lake, cryosphere, megacity etc. The observations are a selected set of important variables covering different processes and concentrations and fluxes of greenhouse gases, trace gases (e.g. CO, ozone, NOx, SO2, VOCs, CH4, NH3, H2SO4, HONO, HNO3) and aerosol particles. The measurements also include several meteorological parameters clouds, atmospheric ions, external radiation, radon, ecosystems, photosynthesis, soil dynamics and vegetation growth, as well as ground-based remote sensing. Right now we are measuring about 1200 different variables in the SMEAR II station. It is crucial to have an open access to observations, open data and data flows. For example SmartSMEAR (Junninen et al., 2009) is an excellent tool to obtain data near real time.

THE VALUE OF SMEAR CONCEPT

The first quantification of the COBACC (CONTinental Biosphere-Aerosol-Cloud-Climate) feedback loop (Kulmala et al. 2004b, 2014a) was based on continuous comprehensive observations at SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations) station in Hyytiälä, Finland, and showed that a 10 ppm increase in atmospheric CO2 concentration leads to a significant (several percent) increase in both carbon sink and aerosol source. These effects operate through changes in gross primary production, volatile organic compound (VOC) emissions and secondary aerosol formation associated with atmospheric oxidation of VOCs. This feedback loop demonstrates how important biospheric processes are not only for carbon and aerosol budgets, but also for the whole climate system. Since the COBACC feedback suppresses global warming, potentially giving the mankind a window of opportunity to reduce global carbon emissions, it is crucial to find out how important this feedback loop is globally and particularly in boreal and arctic environments. The strength of the COBACC feedback is connected tightly with the functioning of the biosphere, including the observed yet poorly-understood greening and other vegetation changes currently taking place in boreal and Arctic environments. Therefore, more knowledge is needed to understand and quantify how the functioning of the biosphere and COBACC feedback loop will develop in the future.

Long-term continuous and comprehensive observations have shown their strength in several ways. One crucial example is observations of regional new particle formation (NPF) events. The longest time series in the world (Nieminen et al., 2014) have given also the basis for our discoveries of the sub 3 nm world in the atmosphere. Altogether, the SMEAR II station has been directly or indirectly the basis for more than 2000 scientific articles, including more than 30 papers published in Nature or Science.

One important example is Gas-to-particle conversion (GTP), which is a key phenomenon for our understanding of processes, interactions and feedbacks between atmospheric chemistry and physics. By producing new aerosol particles and secondary particulate matter, GTP modifies the number concentration, size distribution, chemical composition and mass loading of atmospheric aerosol particle populations, thereby having close associations with both air quality and climate. The GTP taking place below particle sizes of a few nm, termed nano-GTP here, is of special interest because it dictates the contribution of new particle formation (NPF) to the atmospheric aerosol number load.

The traditional view of nano-GTP (Friedlander, 1977) includes three separate steps: 1) chemical reactions in the gas phase to produce low-volatility vapor(s), 2) nucleation and 3) subsequent condensational growth. Until recently, only little effort has been devoted to exploring the gas-phase chemistry responsible for the production of nucleating and condensing vapors. The main reason has been that sulfuric acid, produced via the gas-phase SO2 + OH reaction, was long thought to be the sole important trace gas in this respect. However, several recent findings have shown that this is not necessarily the case (e.g. Bianchi et al. 2016, Kirkby et al. 2016).

Recent progress in measurement methods and theoretical understanding, together with their application in laboratory and field conditions, has brought extensive new insights into atmospheric nano-GTP. As a
result, Kulmala et al. (2014b) revised the traditional view of this process, adding two more steps to make a five-step process: 1) similar to the traditional step 1, but with new oxidation pathways, 2) clustering, 3) nucleation or barrierless nucleation, 4) activation of clusters with a second group of vapors, and 5) similar to the traditional step 3, but now with multicomponent condensation. There are several reasons for including these additional steps. First, the formation of molecular clusters (step 2) appears to take place practically everywhere and all the time, whereas the formation of nanoparticles able to grow by condensation (step 5) clearly takes place under much more specific conditions (Kulmala et al. 2013 and references therein, Kontkanen et al. 2016). Second, there are strong indications that the vapors governing clustering do not usually produce growing nanoparticles, but rather that a second group of vapors is needed to heterogeneously nucleate on small clusters or start to contribute to the growth via nano-Köhler type processes (Kulmala et al. 2004a, Tröstl et al. 2016) (step 4). Third, there are almost certainly vapors that enhance condensation growth but that do not participate in either clustering or activation. Finally, it is still unclear whether there really is a critical size separating growing clusters from other stable atmospheric clusters, or whether the transition from clustering to activation takes place without a significant energy barrier (Kulmala et al. 2013). This question is especially relevant when one considers the huge range of potentially contributing organic compounds. On the other hand, clustering and chemical reactions are also related to each other, as both processes require molecular collisions, and lead either to physical cluster formation or chemical reactions, such as oxidation or oligomerization. In some cases, molecules in physical clusters can react to form larger molecules. This revised nano-GTP scheme (Kulmala et al. 2014b) combines, in a consistent way, atmospheric chemistry and dynamics of molecules, small atmospheric clusters and growing nanoparticles in the process of new particle formation.

Recently-developed instruments, such as the Particle Size Magnifier (PSM, Vanhanen et al. 2011), Chemical Ionisation Atmospheric Pressure interface Time–of-Flight mass spectrometer (CI-API-TOF, Jokinen et al. 2012) and Neutral cluster and Air Ion Spectrometer (NAIS, Kulmala et al. 2007), have proven to be very effective in both laboratory (e.g. Kirby et al. 2016) and atmospheric (Kulmala et al. 2013) investigations. However, in order to truly be able to verify and quantify the different steps in nano-GTP, we must develop our instrumentation even further and apply them in various environments from well-controlled chamber facilities to remote and hard-to-access sites around the planet.

According to our present understanding, sulfuric acid and extremely low volatile organic compounds (ELVOCs; Donahue et al. 2012) are the key compounds in atmospheric clustering (Kulmala et al. 2013, Kirkby et al. 2016, Bianchi et al. 2016). However, before forming new particles (with diameters above 3 nm), sulfuric acid clusters need to be stabilized by other compounds. Likely candidates are gaseous amines, ammonia, ELVOCs, and air ions (Kirkby et al. 2016, Lehtipalo et al. 2016). On the other hand, and also in the case of pure ELVOC clusters, other compounds are needed to help nano-GTP to produce new particles at atmospherically significant rates. This involves some combination of decreasing cluster evaporation rates due to stabilizing agents and increasing particle growth rates boosted by second vapours, as extremely small nano-clusters have very short lifetimes due to collisions with larger particles and thus they meet "grow or die dilemma" before forming new particles. The relative contribution of these cluster-stabilizing agents depends on their atmospheric concentrations. Air ions are a special case in this respect, since they are omnipresent in the atmosphere and therefore almost certainly make a contribution.

OTHER LEGACY AND FUTURE PERSPECTIVES

We have planned and constructed the SMEAR stations to provide continuous information on long-term trends in the aerosols, trace gases and greenhouse gases over boreal forests, combined with information on material and energy flows within the forest-atmosphere continuum, making it possible to test novel theories and instrumental techniques under boreal forest conditions. The common planning and measuring principles at different stations have enabled combination of the data within stations and also between stations. The power of the measurements will increase when more stations join the station network. The common principles, like energy and mass flows provide the common language within the station network and we are able to obtain coherent, comprehensive data sets.
Based on the experience obtained at SMEAR II station we have been able to establish national center of excellences (from 2002) and several Nordic center of excellences from which we made the next step and were invited to lead international Land ecosystem and atmosphere processes study under International Geosphere-Biosphere Programme (IGBP). Later on this was the basis of our Future Earth Activities.

To mention some other legacy we have established summer, winter and autumn schools with participants from more than 50 countries and also to make SMEAR globally over the whole planet we have Global SMEAR initiative.

Starting from 2012 (October) the international Pan-Eurasian Experiment (PEEX) Program (Lappalainen et al., 2014, Kulmala et al. 2015) has been established. The program carries out an extensive multidisciplinary agenda focused on sustainable development of the environments and societies of the Northern high latitudes and of China. As a fundamental part of the program is the constructions of the land-atmosphere in situ station network in Russian and in China, which can contribute to the global observation systems such as Geo Cold Regions Initiative (GECRI) and WMO Global Atmospheric (GAW) Program.

Furthermore, our present international activities besides PEEX like Global SMEAR and contribution to solve air pollution problems in China and other megacities are rapidly ongoing. All of these would not be possible without activities based on SMEAR II observatory.

REFERENCES

HETEROGENEOUS VERSUS HOMOGENEOUS NUCLEATION OF ICE IN THE UPPER TROPOSPHERE AND LOWER STRATOSPHERE

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Keywords: meteoritic dust, mineral dust, glassy aerosols, tropics, extra-tropics.

INTRODUCTION

The nucleation of ice particles in the upper troposphere and lower stratosphere leads to the formation of cirrus clouds and polar stratospheric clouds (PSCs), respectively. The resulting ice particle number densities, and hence the radiative and dehydrating properties of these clouds, depend mainly on the amplitude of small-scale temperature fluctuations, which force the ice nucleation, as well as on the availability of aerosols suitable for homogeneous or heterogeneous ice nucleation. There is compelling evidence for the importance of heterogeneous nucleation, likely on solid particles of meteoritic origin, and of small-scale temperature fluctuations, for the formation of ice PSCs in the Arctic stratosphere. Conversely, in the upper troposphere it is less clear how important solid ice nucleating particles (INPs) are for cirrus cloud formation. We review in situ and remote sensing measurements, laboratory studies and modeling approaches to ice clouds in both the lower stratosphere and upper troposphere. Evidence emerges that in the upper troposphere heterogeneous ice nucleation plays a large role in nucleating very cold, thin cirrus in the upper tropical troposphere, whereas heterogeneous ice nuclei typically cannot effectively compete with homogeneous ice nucleation in the warmer midlatitude upper troposphere.

CIRRUS OBSERVATIONS AND MODELLING

Engel et al. (2014) have analyzed spaceborne lidar observations by CALIOP on CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations) using extensive trajectory and microphysical box model calculations. They reviewed PSC ice formation processes, resulting in clear evidence that widespread synoptic-scale ice clouds could not be explained solely by homogeneous ice nucleation. The required efficiency of the ice nuclei—probably of meteoritic origin—is surprisingly high, namely comparable to that of the best known tropospheric ice nuclei such as certain mineral dust particles. Furthermore, to gain model agreement with the ice number densities inferred from observations, the presence of small-scale temperature fluctuations, with wavelengths unresolved by the numerical weather prediction models, is required.

Conversely, it is less clear how important solid ice nucleating particles (INPs) are for cirrus clouds in the upper troposphere (Hoyle et al., 2005; Krämer et al., 2009; Jensen et al., 2013; Cirisan et al., 2014). The earlier of these studies are based on measurements by older cloud probes, suggesting frequent occurrence of ice concentrations greater than 1 cm$^{-3}$. However, it has been shown that ice number density measurements made with the older airborne cloud probes may be exaggerated by shattering artifacts (McFarquhar et al., 2007; Jensen et al., 2009; Korolev et al., 2011).

As an example, Figure 1 shows a comparison of cirrus cloud extinctions derived from lidar backscatter measurements and column model simulations. Extinctions derived from CALIOP backscatter measurements of cirrus clouds observed on all orbits in July 2008 cannot be well reproduced in
simulations with the Zurich Optical and Microphysical Model (ZOMM), when the ice is allowed to nucleate only homogeneously in solution droplets consisting of ammonium sulfate or sulfuring acid (and some organic species), as they are typical for upper tropospheric aerosols. Errors are particularly large for the lowest temperatures.

A significant improvement can be achieved when assuming the presence of heterogeneous nuclei as they had been indicated by the PSC work cited above, however assuming ice nuclei number densities to be lower by one order of magnitude compared to stratospheric condition, e.g. in the course of mixing of this air into the uppermost troposphere. Still, the calculations shown in Figure 1 assume 800 L⁻¹ of these potent ice nuclei, i.e. a very high number.

Figure 1. Comparison of cirrus cloud extinctions derived from lidar backscatter measurements and column model simulations. (a) Extinctions ($\lambda = 532$ nm) derived from CALIOP on CALIPSO for cirrus clouds on all orbits in July 2008 (derived from the backscatter measurements assuming a lidar ratio of 20). (b) Simulation of these cirrus clouds with the Zurich Optical and Microphysical Model (ZOMM) employed as column model including sedimentation and nucleating homogeneously in typical upper tropospheric solution aerosols. (c) Same as (b) but including heterogeneous ice nucleation on potent ice nuclei of meteoritic origin with a number density of 0.8 cm⁻³.
LABORATORY WORK ON MINERAL DUSTS AS ICE NUCLEI

While it is quite likely that the ice nuclei causing synoptic-scale ice PSC formation in the Arctic stratosphere are indeed of meteoritic origin (Murphy et al., 1998), in situ analysis of these particles in the polar winter stratosphere or upper troposphere is still lacking. However, there is clear indication that the solid inclusions in the stratospheric H$_2$SO$_4$/H$_2$O aerosol, which cause the synoptic-scale ice PSCs must be very efficient ice nuclei (Engel et al., 2014), possibly comparable with the most potent mineral dusts, such as feldspars (Atkinson et al., 2013), which were found to be present in many natural dust samples (Kaufmann et al., 2016). In particular microcline (KAlSi$_3$O$_8$) was found to be an exceptionally good ice-nucleating mineral, superior to other analysed K-feldspars, (Na, Ca)-feldspars, and the clay minerals (Kaufmann et al., 2016).

Direct electron-microscopic observations of deposition growth of aligned ice crystals on feldspar has recently shed light on the molecular processes on K-feldspar surfaces (Kiselev et al., 2017). What remains unclear is how atmospheric aging processes change the surface properties of the mineral dusts. We will show that aging processes do not always lead to a deterioration of the ice nucleation ability, but may under certain circumstances also lead to their enhancement.

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REFERENCES


8-HOURS STUDY OF HEAT TRANSFER IN SAUNAS OVER 21 YEARS

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Keywords: Sauna, latent heat, stable water isotope, sauna effect

Once you are in a sauna, especially in the group of physicists, the common discussion topic is “What exactly causes the temporary heat pulse that we feel when we throw some water on the hot stones?” There are probably several reasons but according to my own theoretical analysis the secret is in the latent heat released in the condensation of water vapour onto the skin. The reason is that our skin is most probably the coldest place in the sauna, and the humidity can easily become 100% near the skin after the humidity is increased because of the thrown and evaporated water on the stones.

The first analysis goes back to the ICNAA conference 1996 in Helsinki (Vesala, 1996). After that one working day (about 8 hours) has been devoted by me and my colleagues to study and write on the topic. Data on skin temperatures was collected by infrared sensors during the field course on micrometeorology at Hyytiälä Forestry Field Station (Heikkilä et al., 2011). However, till that moment everything has been just educated speculation with some support from observations without a direct measurement of the condensed water on the skin (Hermans and Vesala, 2007). But then appeared a breakthrough by a German group of scientists (Zech et al., 2015), who conducted sauna experiments. They used isotopically labeled ($^{18}$O and $^{2}$H) water as tracer to distinguish the proportion of condensation water versus sweat, without me knowing anything on it. Cool! The results corroborated the earlier theoretical considerations: the latent heat flux (by condensation) is likely the most important mechanism for the heat pulse that we feel when water is poured on the stones of the sauna stove. Even cooler!

Note that in the atmosphere a similar kind of energy pump is acting at a bit larger scale: evapotranspiration (ET) from the Earth surface is followed by condensation in the formation of tropospheric clouds. This is a very important contribution to atmospheric energy transport and balance. Earth surface, especially stomata on plant leaves, mimics the hot stones and cloud condensation nuclei mimic human skin. I suggested 21 years ago to call the atmospheric ET-cloud condensation energy pump as “Sauna effect”, similarly to “greenhouse effect”. However, I have not noticed any usage of that concept, although the usage of the greenhouse effect is even incorrect for the warming due to greenhouse gases (greenhouse not keeping warm because of absorption of long-wave radiation but being mechanical shelter against wind). Is the time now ripe for the sauna effect?

REFERENCES


ATMOSPHERIC NUCLEATION IN URBAN SHANGHAI

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Keywords: NEW PARTICLE FORMATION, URBAN ATMOSPHERE, NUCLEATION MECHANISM.

INTRODUCTION

Atmospheric nucleation and new particle formation represent, in terms of number concentration, the largest source of atmospheric aerosol particles. Our understanding on the mechanisms for atmospheric nucleation and new particle formation in the pristine atmosphere has improved significantly in the past several years, whereas those under urban environments remain largely elusive. Here we measured the particle number size distributions in the range of 1.34-615 nm between March 2014 and February 2016. Nucleation parameters including nucleation frequency, nucleation rates, growth rates, and condensation sink are statistically connected to meteorological ones and atmospheric trace gases to gain potential impacting factors for urban nucleation. In addition, chemical composition of neutral and charged atmospheric clusters were determined using an Aerodyne high resolution time-of-flight mass spectrometer during the nucleation events. Potential mechanisms for the observed new particle formation events will be discussed.

METHODS

Nucleation measurements were carried out on the rooftop of a teaching building (31°18’N, 121°30’E) that is about 20 m above ground on the campus of Fudan University between March 2014 and February 2016. This monitoring site is mostly surrounded by commercial properties and residential dwellings. The Middle Ring Road, one of main overhead highways in Shanghai, lies about 100 m to the south of the site. Hence, the Fudan site can be treated as a representative urban site influenced by a wide mixture of emission sources (Ma et al., 2014; Wang et al., 2016; Xiao et al., 2015).

Ambient particle size distributions in the range of 1.34-615 nm were measured using a combination of one nano Condensation Nucleus Counter system (model A11, Airmodus, Finland), one nano-SMPS (consisting of one DMA3085 and one CPC3776, TSI, USA), and one long-SMPS (consisting of one DMA3081 and one CPC3775, TSI, USA). The instruments were continuously running except for maintenance and minor instrument breakthrough during the campaign.

During January and February 2016, an Aerodyne high resolution time-of-flight mass spectrometer (Bertram et al., 2011) was deployed at the same site to measure the chemical composition of neutral and charged clusters during the nucleation. Measurements with both chemical ionization using nitrate reagent ions (Ehn et al., 2014) and atmospheric pressure interface mode for ions (Junninen et al., 2010) were carried out to gain insights into the nucleation mechanisms.

CONCLUSIONS

Frequent atmospheric new particle formation events were observed during the campaign, especially in spring and winter. The nucleation rate was the highest in spring whereas the growth rate of newly formed
particles was the largest in summer, hinting that the dominant precursors for nucleation and subsequent growth might be different. A variety of neutral and charged molecules and clusters were detected by mass spectrometry, including sulfur-oxygen-based species, nitrogen-containing species, and organics.

![Figure 1. New particle formation frequency between March 2014 and February 2015.](image1)

![Figure 2. Mass defect plot for neutral species in a new particle formation event on January 23, 2016.](image2)

ACKNOWLEDGEMENTS

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REFERENCES


SESSION 1:
PARTICLE PHASE CHANGE

Bastien Radola: A molecular dynamics study of the phase changes of organic aerosols

Ari Laaksonen: The adsorption theory of heterogeneous nucleation: comparison to experiments

Markus Petters: Phase transitions of intenally-mixed amorphous aerosols

Benjamin Thomas: Oxidation of mixed fatty acid monolayers on an aqueous subphase: Evident for surface phase changes?

Taina Yli-Juuti: Evaporation of α-pinene derived SOA particles under different humidity conditions

Thomas Koop: Glass formation in mixed organic/organic and inorganic/organic aerosol particles
A MOLECULAR DYNAMICS STUDY OF THE PHASE CHANGES OF ORGANIC AEROSOLS: MIXED FORMIC AND ACETIC ACID NANOPARTICLES INTERACTING WITH WATER

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Keywords: organic aerosol, water adsorption, phase change, molecular dynamics.

INTRODUCTION

Aerosols formed by carboxylic acids represent a significant fraction of the total organic matter in the atmosphere. These aerosols, which are often characterized by an intricate composition, generally have carboxyl groups and free hydroxyls on their surface that can form hydrogen bonds with surrounding water molecules. Organic aerosols are thus suspected to be effective condensation nuclei for water molecules in the atmosphere. The importance of such aerosols on the physico-chemistry of the atmosphere therefore requires a better understanding of their interaction with the surrounding water molecules, to which studies at the molecular level can contribute.

METHODS

In the present work, we have used Molecular Dynamics (MD) simulations to study the phase changes of small organic acid aggregates interacting with water. Aerosols have thus been modeled by binary aggregates of formic and acetic acids interacting with variable amounts of water molecules representing different relative humidity levels. In order to study the influence of temperature, calculations have been carried out in the \((N, V, T)\) ensemble with a temperature range of 150 K to 275 K. Formic acid and acetic acid models have been taken from the OPLS-AA force field, and water molecules have been represented by the four-sites TIP4P/2005 model.

Figure 1: Snapshot of a 4:1 water–acid ratio aggregate as modeled in our simulations at a temperature of 150 K (left) and 275 K (right). The 4:1 water–acid ratio system contains 350 acetic acid, 350 formic acid and 2800 water molecules.
CONCLUSIONS

Our results showed that both the temperature and the water content have an influence on the structure of the systems. Different phases have been evidenced, corresponding to a large acid core surrounded by water at low temperatures (∼150 K), or a water droplet with acid molecules adsorbed at the surface at higher temperature (typically above 225 K) and high water content. A mixed phase was obtained at intermediate temperatures and at low water content, corresponding to a partial deliquescence of the acid aggregate and a mixing of acid and water molecules.

Moreover, a slight difference in the behavior of the two acid species was also observed that can be related to the length of the hydrophobic hydrocarbon chain. Indeed, for systems corresponding to water droplet coated by acid molecules, it was found that formic acid molecules were evenly distributed between the aqueous phase and the acid coating, whereas acetic acid molecules were located almost exclusively at the surface of the water–acid aggregates. The comparison with the results obtained from simulations of single acid aggregates interacting with water (Vardanega, 2014; Radola, 2015) indicate that formic acid–acetic acid interactions do not play a significant role in the mixed acid systems.

Figure 2: Average size of clusters formed by chains of formic acid (left) and acetic acid (right) molecules in the simulated aggregates as a function of the temperature for 0:1, 1:1, 2:1, 4:1 and 8:1 water–acid ratios.

The present results represent an additional step toward modeling of organic Cloud Condensation Nuclei (CCN), leading to a deeper understanding of the heterogeneous nucleation of water, in the environmentally relevant context.

ACKNOWLEDGEMENTS

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REFERENCES


THE ADSORPTION THEORY OF HETEROGENEOUS NUCLEATION: COMPARISON TO EXPERIMENTS

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Keywords: Adsorption, Heterogeneous nucleation, Ice nucleation

INTRODUCTION

The deficiency of the classical nucleation theory (Fletcher, 1958) in predicting critical supersaturations for heterogeneous nucleation is well known. We have recently developed a new theory that describes vapour adsorption at sub-saturation and heterogeneous nucleation at supersaturation as a continuum rather than as separate phenomena (Laaksonen, 2015; Laaksonen and Malila, 2016). Here, we review the predictive success of the new theory against experiments of both water and (deposition) ice nucleation on a number of different substrates.

THEORY

The adsorption nucleation theory (Laaksonen, 2015; Laaksonen and Malila, 2016) offers a means to extrapolate a measured adsorption isotherm to the supersaturated regime and to find the critical supersaturation for heterogeneous nucleation in a reliable way.

The basic idea of the new theory is to combine the multilayer Frenkel-Halsey-Hill (FHH) adsorption isotherm, and the Kelvin equation. The FHH isotherm gives adsorption layer thickness at given water vapour saturation ratio when two FHH parameters (A and B) are known. On non-wettable surfaces, the adsorption layer is not homogeneous but consists of small droplets (Cao et al., 2011), and the Kelvin equation describes how vapour pressure is increased over the droplet surfaces compared to a flat adsorption layer. Beside the A and B –parameters (that describe the interaction between the substrate and the first adsorption layer, and the decay of the interaction as a function of distance in subsequent layers, respectively), the theory contains two more parameters: the contact angle Θ, and the average distance between adsorption sites s. When Θ and s are known, the sizes of adsorbed droplets can be related to the macroscopically observable adsorption layer thickness. In practice, the contact angle needs to be measured separately, and A, B, and s can be obtained from adsorption measurements.

When the four parameters of the theory are known, a curve of adsorption layer thickness (or alternatively, diameter of adsorbed droplets) can be drawn as a function of water vapour saturation ratio. Because of the Kelvin effect, the curve extends to the supersaturated region, where it exhibits a maximum. Similarly as with Köhler theory of cloud drop formation, the maximum signifies the critical supersaturation for heterogeneous nucleation. Note, however, that in cases with small average distance between adsorption sites, coalescence of adsorbed droplets can initiate nucleation already at some lower supersaturation.
RESULTS

<table>
<thead>
<tr>
<th>Nucleus type</th>
<th>Particle size</th>
<th>Contact angle</th>
<th>$S^<em>_{\text{Th}}/S^</em>_{\text{Exp}}$ AT</th>
<th>$S^<em>_{\text{Th}}/S^</em>_{\text{Exp}}$ CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame soot</td>
<td>15 – 60 nm</td>
<td>0°</td>
<td>0.97</td>
<td>3.16</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>25 – 90 nm</td>
<td>16°</td>
<td>0.58</td>
<td>4.47</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>20 – 120 nm</td>
<td>20°</td>
<td>1.20</td>
<td>2.28</td>
</tr>
<tr>
<td>Montmorillonite$^1$</td>
<td>100 – 800 nm</td>
<td>22°</td>
<td>1.10</td>
<td>3.86</td>
</tr>
<tr>
<td>Illite$^1$</td>
<td>100 – 800 nm</td>
<td>24°</td>
<td>0.89</td>
<td>1.93</td>
</tr>
<tr>
<td>Quartz$^1$</td>
<td>Supermicron</td>
<td>36°</td>
<td>1.43</td>
<td>3.85</td>
</tr>
<tr>
<td>Calcite$^1$</td>
<td>Supermicron</td>
<td>42°</td>
<td>0.91</td>
<td>3.14</td>
</tr>
<tr>
<td>Plexiglass</td>
<td>Flat surface</td>
<td>80°</td>
<td>0.83</td>
<td>2.97</td>
</tr>
<tr>
<td>Spark soot</td>
<td>20 – 100 nm</td>
<td>82°</td>
<td>0.83</td>
<td>11.00</td>
</tr>
<tr>
<td>Ag$_2$O</td>
<td>6 – 18 nm</td>
<td>90°</td>
<td>0.72</td>
<td>3.86</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td><strong>0.95</strong></td>
<td><strong>4.05</strong></td>
</tr>
</tbody>
</table>

$^1$Ice nucleation

Table 1. The ratios of theoretical to experimental critical supersaturations for the adsorption nucleation theory (AT) and classical nucleation theory (CNT). The ratios presented in the table are averages over the particle sizes shown in column two.

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REFERENCES


PHASE TRANSITIONS OF INTERNALLY-MIXED AMORPHOUS AEROSOLS

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Keywords: aerosol phase, organic aerosol, mixing rules, aerosol viscosity.

INTRODUCTION

The phase state of atmospheric aerosol affects a wide range of processes, including optical properties, droplet and ice nucleation rates, gas-particle exchange rates, and condensed-phase chemical reaction rates. Recent laboratory and field experiments have shown that organic aerosols can exist in amorphous semi-solid or glassy phase states at room temperature. The phase state and the related particle viscosity is determined by the particles’ chemical composition. Specifically, the number and type of oxygenated organic functional group are important determinants of the viscosity (Rothfuss and Petters, 2017a). Viscosity also strongly depends on temperature ($T$) and relative humidity (RH) (Rothfuss and Petters, 2017b).

Amorphous phase state diagrams (Rothfuss and Petters, 2017b) can be used to assign the phase state of organic aerosol over a wide range of $T$ and RH. The phase diagram shows a clear demarcation between liquid and glassy states and permits quantification of aerosol viscosity in the semi-solid regime ($10^4$ to $10^{12}$ Pa · s). Amorphous phase state diagrams of organic aerosol with multiple components, including those where one component is an inorganic salt, have not been reported in the literature. This work presents such phase diagrams for internally mixed sucrose-citric acid and sucrose-sodium nitrate aerosol.

METHODS

Viscosity was measured using the coalescence time-scale technique applied to ≈100 nm diameter particles that were prepared by atomization. Coalescence was induced by coagulation of mobility-selected particles carrying opposite charges, followed by isolation of the charge neutral dimers via electrostatic filtration (Rothfuss and Petters, 2016). Full or partial coalescence of the dimers was measured as a function of $T$ and RH using shape factor analysis on the size distribution produced by a scanning mobility particle sizer (Rothfuss and Petters, 2016; Rothfuss and Petters, 2017b).

SUMMARY

The temperature dependent viscosity data are used in conjunction with RH relaxation data, aerosol hygroscopicity, Vogel-Fulcher-Tammann temperature dependence, and ternary mixing rules to construct a phase state model for internally-mixed aerosols.
ACKNOWLEDGEMENTS

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REFERENCES


OXIDATION OF MIXED FATTY ACID MONOLAYERS ON AN AQUEOUS SUBPHASE: EVIDENCE FOR SURFACE PHASE CHANGES IN ATMOSPHERIC AEROSOL?

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Keywords: SURFACE, MONOLAYER, OXIDATION

SUMMARY AND ABSTRACT

Fatty acids, amongst many other insoluble or near-insoluble organic compounds, partition to the air-aqueous interfaces present all over the earth (Donaldson, 2006). The presence of these layers at the boundary between atmospheric aerosol droplets and the surrounding atmosphere has a huge variety of effects on the behaviour of the water droplet itself, the ageing and reactions of the components of the film (compared with behaviour in a bulk state), and even on the rate and nature of atmospheric reactions that require partition of reactants into the water droplet or onto the air-water interface (Donaldson, 2006). These effects could have huge knock-on importance for the interaction of aerosols with the climatic functions of clouds, an interaction which is complex and only partially understood (Stevens, 2009). Such interactions are the largest single source of uncertainty in climatic predictions (IPCC, 2013).

Our research consists of the study of the ageing of these layers under exposure to ozone (O₃) and nitrate radicals (NO₃). We are focusing on studying multi-component monolayers, using a novel combination of Neutron Reflectometry (NR) and Fourier-Transform Infra-Red Reflection Absorption Spectroscopy (FT-IRRAS) to compare the behaviour of these more complex systems with the behaviour of simpler mono-component films.

Part of our study has involved investigating the reactivity of the well-characterised oleic acid (OA) / ozone system when that OA monolayer is co-deposited along with an unreactive fatty acid in a mixed monolayer with which it is immiscible. We have experimented using both stearic and palmitic acids as the unreactive component. When stearic acid (SA) is used as the unreactive component, results from our NR/FT-IRRAS coupled setup, which is intended for measuring the surface concentrations of the reactive and unreactive components at kinetic resolutions, were confounding and unexpected. We observed, when using NR to measure SA, an apparent increase in SA surface concentration as the concentration of OA dropped away as expected under oxidation. When the analysis was reversed, and FT-IRRAS was used to measure SA, the concentration of SA appeared to fluctuate.

We interpret these signals as indicating a phase change in the monolayer film at the surface as oleic acid is removed by oxidation. FT-IRRAS is very sensitive to molecular orientation at the interface, and changes to this disturb the correlation between IR signal and surface concentration, whereas the apparent increase in NR signal could also indicate a phase change, as the presence of domains in the size order of tens of microns or larger (as observed in previous Brewster Angle Microscopy work (Sebastiani, 2014)) in the initial multi-component film would cause an under-estimation in the surface concentration of the material in question by a model which assumed uniform coverage. The disappearance of these domains during the phase change initiated by the oxidation of the co-deposited oleic acid domains would remove this confounding factor, leading to an apparent increase in concentration of the relevant compound.
BACKGROUND AND INTRODUCTION

The presence of insoluble films at the interface between a water droplet and the atmosphere has a number of consequences that are of utmost importance for atmospheric chemistry. Most simply, these films can act as a barrier to mass transport between the water droplet and the atmosphere. Multiple studies have shown that insoluble films at the interface are able to significantly retard both the evaporation of the water droplet itself and the transport of oxygen (O₂), ozone (O₃), ammonia (NH₃), and many other important atmospheric species between the water droplet bulk phase and the atmospheric bulk phase (e.g. Barnes, 1997). This inhibition of cross-interfacial transport could hinder the progress of atmospheric reactions that are carried out inside water aerosols and thus rely heavily on mass-transport steps across the air-aqueous boundary (Daumer, 1992).

Conversely, the surface film itself can act as a ‘2D solvent’ for species from the atmosphere, thus allowing the dissolution of species that would not normally dissolve in a water droplet, or altering the solvation behaviour of species that normally would dissolve in the droplet (Gilman, 2004). This effect may play an important role in the transport of various species by water droplets, as it allows species that would not normally be transported by water droplets to be adsorbed at the coated interface and transported thus (Donaldson, 2006). These changes in solvation behaviour at the interface will have severe knock-on effects on the rates and even natures of atmospheric reactions that occur heterogeneously at the interface of such particles. Studies of some reactions have shown a reduction in reaction rates, such as the rate of the production of nitric acid (HNO₃) from dinitrogen pentoxide (N₂O₅) and water (Folkers, 2003), (a key atmospheric process for the redistribution of nitrogen amongst various species in the atmosphere) as a result of the presence of these coatings (Donaldson, 2006). The complexity of this effect is demonstrated by the existence of cases in which the complete opposite is true (situations in which organic coatings enhance heterogeneous reaction rates), such as the case of halide proton exchange reactions (Lawrence, 2005).

These films are often reactive themselves. Reactions of these films with atmospheric oxidants such as ozone (O₃), nitrate radicals (NO₃), and hydroxyl radicals (OH), and the way in which these reactions differ from the interactions between bulk samples of the substances comprising these films with the aforementioned atmospheric oxidants, form the basis of this research. Oleic acid has been established as a benchmark system for long-chain fatty acids (Donaldson, 2006), and work by King et al (2009) has established the reactivity of the monolayer of oleic acid system.

These films could also have critical meteorological effects. All sorts of cloud formation, growth, evaporation, and rainout processes have a critical dependence upon surface tension. This is part of the fundamental nature of the behaviour of water droplets in the atmosphere (Ambaum, 2010). The presence of insoluble organic films at the air-aqueous interface has a severe effect on the surface tension of the resultant water aerosols, and the knock-on effects in terms of interactions with clouds, and with cloud aerosol lifetime effects, is only just beginning to be understood (Donaldson, 2006), with two major recent studies coming to opposite conclusions about the nature of this interaction (Abbatt, 2005; Sorjamaa 2004).

The body of research available on this topic, the surface of which is only barely scratched by this introduction, contains many contradictory conclusions and differing perspectives on the importance of these various effects.

Insoluble organic films at the air-aqueous boundary also notably alter the reactivity of the water droplets themselves, affecting the formation of clouds and impinging upon all the climatic feedback and forcing processes in which they are involved, as well as altering the reactivity of the material making up the film itself (the subject of this research), and altering the rate and nature of reactions that can occur inside the droplet and on its surface.
METHOD AND EXPERIMENTAL

Our novel experimental setup allows for the deployment of an FT-IRRAS mirror setup on the NR beamline ‘INTER’ at the ISIS neutron facility. A bespoke reaction chamber presents the monolayer, which is deposited from a CHCl₃ solution, upon a subphase of Air Contrast Matched Water (ACMW — partially deuterated water that does not reflect neutrons), to a controlled atmosphere in which the concentrations of oxidants can be varied by a gas production and flow setup. The reaction chamber includes quartz windows (invisible to neutrons) on one pair of vertical faces to allow ingress and egress of the neutron beam, and CaCl₂ (invisible to mid-IR) windows set at a 48 degree angle from vertical and orthogonal to the quartz windows to allow ingress and egress of the IR beam. See Figure 1 for a visual representation.

![Diagram of the experimental setup](image)

Figure 1 - NR/FT-IRRAS Oxidation Setup: Neutron path in grey; IR photon path in turquoise; Oxidant gas flow in blue; Oxidation cell walls in red; Quartz windows in green; CaF₂ windows in purple.

The multi-component film is the selectively deuterated so that one of the components has a high deuterium concentration and contrasts heavily with the other components in the system for NR measurement. The reflectivity data are then fitted to a monolayer coverage model and the concentration of the deuterated component at the interface is determined. The IR system is used to examine absorbance bands accounted for by vibrational modes of C-D and C-H bonds, allowing for semi-quantitative tracking of both the deuterated and non-deuterated components.

The well-established technique of Brewster Angle Microscopy (BAM) for visual analysis of surface domains and the use of Langmuir troughs with movable barriers and a pressure sensor to measure surface tensions also play a part in this research.

RESULTS AND CONCLUSION

The OA/SA system was studied under oxidation by O₃ in both possible selective deuteration configurations, and the results show unusual behavior of the SA component after OA oxidation that suggest a phase change. The existence of microscale domains in this immiscible system has already been established in previous BAM work by Sebastiani (2014). OA was seen to react with O₃ in a manner consistent with a 2nd-order surface reaction, considering [O₃]surf as deducible from [O₃]gas via a dimensionless Henry's Law solubility constant of 11.7 (deduced from a value reported by Smith et al (2002) in pressure/concentration units). SA concentrations were seen to increase when studied with NR (Figure 2) and were seen to fluctuate when studied with FT-IRRAS (Figure 3).
Our conclusion from these results is that a phase change in the monolayer film at the surface is occurring during the oxidation of oleic acid and its concurrent loss from the surface monolayer. The FT-IRRAS signals from SA indicate a phase change as the concentration of SA at the surface is very unlikely to change (SA does not react with O₃ as it has no double-bond) and therefore the signal changes are likely due to changes in molecular orientation or island distribution. The increase in NR signal also points towards a phase change, as domains of an order of longer than the neutron coherence length (order of tens of microns) will result in an under-estimation of coverage will cause an under-estimation of coverage by a model with assumes a homogenous surface. BAM work by Sebastiani (2014) confirms the existence of these domains, and the increase in apparent coverage that we observe upon oxidation is likely due to their disappearance.

An application to study this effect in more detail, and to see if it applies to other, similar immiscible systems (one exploratory run with palmitic instead of stearic acid suggested it does not) has been accepted by the ISIS neutron and muon source, and the work will take place at the end of March. This, when combined with further FT-IRRAS work planned for February and March, will hopefully allow us to study this intriguing effect in greater detail. Further work currently underway using Langmuir troughs with movable barriers coupled to a surface pressure sensor will also allow us to deduce the surface phase before the reaction in more detail, and will allow us to determine is this effect is seen when reacting from a starting position of a particular surface phase, or if it occurs in all surface configurations.

REFERENCES AND BIBLIOGRAPHY

EVAPORATION OF α-PINENE DERIVED SOA PARTICLES UNDER DIFFERENT HUMIDITY CONDITIONS

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Keywords: SOA, VOLATILITY, VISCOSITY, VBS.

INTRODUCTION

Large fraction of atmospheric aerosols is formed in the atmosphere as a result of oxidation of volatile organic compounds (Hallquist et al., 2009). This secondary organic aerosol (SOA) consists of numerous compounds with varying properties – many of which are currently poorly known. Knowledge on the formation and transformation of atmospheric SOA particles are needed for improving presentation of aerosol climate effects in global models.

Gas-particle partitioning of organics changes both the composition and size of atmospheric aerosol particles. This partitioning is highly dependent on the saturation vapor concentrations (C*) of SOA constituents, and parameterizations for C* distribution of SOA have been developed based on SOA growth experiments. α-Pinene is among the main precursors for atmospheric SOA, and, therefore, SOA derived from oxidation of α-pinene is often used as a model system for atmospheric biogenic SOA. Vaden et al. (2011) and Wilson et al. (2015) found that SOA particles formed in ozonolysis of α-pinene evaporate slower than expected based on the volatility basis set (VBS) parameterization derived from SOA growth experiments. Semi-solid phase state of the SOA particles has been suggested as a possible reason for the reduction of evaporation rate; The diffusivity of evaporating molecules within the particle phase may be limiting the evaporation rate of a viscous particle. Other possible reasons include uncertainties in the VBS parameterization. For instance, extremely low-volatile compounds, that are not included in the previous C* parameterizations, have been detected in gas phase (Ehn et al., 2014) and they are likely present also in the particle phase. Additionally, vapor wall losses may affect SOA experiments and cause uncertainty in derived SOA properties (Kokkola et al., 2014).

Here we investigate the evaporation of α-pinene derived SOA particles at constant temperature under dry and humid conditions. We analyze laboratory experiments using kinetic evaporation model, and we focus on the roles of the particle viscosity and the volatility distribution of SOA constituents.

METHODS

SOA was generated in a continuous flow tube reactor by ozonolysis of α-pinene. The formed SOA was first passed through an ozone scrubber and then led to a differential mobility analyzer (DMA) for size selection. The monodisperse (diameter 80 nm) particle population was led to a stainless steel chamber (100 L) where the particles started to evaporate due to the dilution of gas phase at the DMA. The particles were sampled from the evaporation chamber for size measurements during the filling. After filling, the
chamber was closed, and later the sampling was resumed after certain periods. This allowed for investigation of particle evaporation up to few hours. Alternatively, evaporation chamber was bypassed and the particles were sampled from the DMA through stainless steel tubing providing short residence times (2-130 s). Particle size was measured with a Scanning Mobility Particle Sizer (SMPS) and the chemical composition was measured with a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, hereafter AMS). Gas phase concentration of α-pinene was monitored with a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS). The conditions in flow tube were similar in each experiment. To enable investigation of SOA particle evaporation under different humidity, the sheath flow in the DMA and the evaporation chamber were conditioned to either dry, 40% RH or 80% RH. All experiments were carried out at room temperature.

The measured evaporation rates (i.e. the particle diameter as a function of time) under different humidity were interpreted using two kinetic evaporation models. Organic compounds were presented with an 8-bin 1D VBS (Donahue et al., 2006). Values of C* for the bins were $10^{-2}$-$10^{4}$ μg m$^{-3}$. In both models, the evaporation of organics was presented as kinetic process; however, water uptake by the particles was calculated assuming an ideal solution and constant instantaneous equilibration between gas phase and particle surface. The first model, the evaporation model for liquid-like particles, assumes that particles are well mixed. This model was used for analyzing the evaporation under 80% RH, where the viscosity of α-pinene SOA particles is relatively low (Rembaum-Wolff et al., 2013). The initial particle composition (described by the C* mass distribution) was determined by fitting the liquid-like particle model to the measured evaporation curve at 80% RH. As the particles were formed under same conditions in each experiment, the derived initial organic composition can be assumed to hold also for the evaporation experiments under dry and 40% RH conditions. The second model, the kinetic multi-layer model (a modified version of KM-GAP; Shiraiwa et al., 2012; Shiraiwa et al., 2013), includes presentation of molecular diffusion inside the particles and, therefore, takes into account the effect of particle phase viscosity. This model was applied for the dry and 40% RH experiments together with different assumptions of particle viscosity.

RESULTS AND CONCLUSIONS

Evaporation of the particles was much slower under dry conditions compared to 80% RH (Figure 1a). At 40% RH the particles evaporated slightly faster compared to 80% RH. The presence of water in the particles under humid conditions would be expected to slow down the evaporation compared to dry conditions, if the only difference between the humidity cases was the Raoult’s solution effect. Our results suggest that the presence of water had also other effect than the decrease of equilibrium concentrations as a results of dilution of a solution particle.

Based on our modelling results at 80% RH, a large fraction of the particle mass at the beginning of the evaporation consisted of low-volatile compounds with C* ≤ $10^{-2}$ μg m$^{-3}$ (Figure 1b). During the evaporation, the more volatile compounds evaporated first and only the least volatile compounds were left in the particle phase at the end of the experiment. Based on the constant measured O:C ratio, the low-volatile compounds were not highly oxidized. Instead, they were possibly dimers with similar O:C ratio as the more volatile constituents.

A possible explanation for the observed change in evaporation rate with humidity is that the increased viscosity of particles at lower humidity conditions slows down the evaporation. To produce the observed evaporation curve with the evaporation model, we needed to assume a strongly composition dependent viscosity for the particles at dry and 40% RH conditions. As the mass fraction of the least volatile compounds increased along the evaporation, the viscosity increased up to approximately $10^{8}$ Pa s under dry conditions and $10^{4}$ Pa s under 40% RH. Despite of the high viscosity, the effect of viscosity on the rate of evaporation was small at 40% RH. Therefore, at 40% RH we can not exclude the possibility that uncertainties related to water uptake calculations or experimental methods would explain the difference in measured and modelled evaporation rate without any viscosity effect. Our analysis shows that the
evaporation at 40% RH can be captured with a liquid-like evaporation model by assuming a rather small deviation to the determined initial particle volatility distribution. Similar dependence in evaporation rates respect to humidity was observed for SOA particles generated by OH oxidation of α-pinene under varying oxidation conditions. Our results suggest that dynamics of α-pinene derived SOA particles in laboratory experiments carried out under dry conditions may be influenced by mass transfer limitations inside the particles. Under atmospherically relevant humidity conditions the effect of particle viscosity was minor for the studied particles.

Figure 1. Panel a presents the measured particle evaporation curves (diameter divided by the initial diameter as a function of time) for dry and 80% RH experiments. Included are also the model predictions at 80% RH based on the best fit initial particle composition (shown in panel b) and the model predictions at dry conditions assuming low viscosity (blue dashed line) or composition dependent viscosity which reaches values up to approximately $10^9$ Pa s (solid blue line).

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REFERENCES


GLASS FORMATION IN MIXED ORGANIC/ORGANIC AND INORGANIC/ORGANIC AEROSOL PARTICLES

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Keywords: GLASS TRANSITION, PHASE SEPARATION, EFFLORESCENCE

INTRODUCTION

The formation of an amorphous solid (glassy) state of condensed matter has been an active field of research in fundamental material science for decades. More recently, it has become clear that also atmospheric aerosol particles may form glasses at dry conditions (Virtanen et al., 2010). For example, secondary organic aerosol (SOA) particles from different precursors have been shown to become amorphous semi-solids or amorphous solids. These observations are supported by laboratory experiments with SOA surrogate compounds, i.e. oxidation products of α-pinene such as pinonic acid and 3-methylbutane-1,2,3-tricarboxylic acid (3-MBTCA). It has been shown experimentally that 3-MBTCA transforms into a glass already above room temperature (Dette et al., 2014). These observations imply that highly viscous or glassy states may exist in SOA particles, which may significantly affect the aerosol particles’ chemical reactivity as well as their physical properties such as water uptake.

There are, however, also a number of open questions: How does uptake of water affect glass formation of different types of organics? How do multicomponent organic mixtures form glasses? And how is the glass transition of organics affected by mixing with inorganic electrolytes? To answer these leading questions, we present new experiments of glass transition temperatures of various mixtures of organics with water and other organics, as well as of organics with inorganic electrolytes.

METHODS

The classical method of determining the temperature at which a glass transforms into a viscous liquid is differential scanning calorimetry (DSC). For that purpose a crystalline sample is first heated to above its melting temperature and thereafter cooled to low temperature. If crystallization can be avoided the liquid transforms into a glass and the glass transition temperature $T_g$ can be determined in the second heating cycle. If nucleation of the crystal occurs, however, the glass transition cannot be determined. Hence it is favorable to study very small samples such as aerosol particles which do not crystallize readily. Another caveat is the fact that many organics decompose upon melting thus preventing $T_g$ measurement.

In order to circumvent the above experimental problems, we have developed a new experimental technique termed MARBLES (Metastable AeRosol By Low temperature Evaporation of Solvent) which combines aerosol production, diffusion drying, and particle collection by impaction (Dette et al., 2014). MARBLES avoids the requirement for heating above the melting temperature by
dissolution of the substance of interest in water and subsequent diffusion drying of aerosolized particles at room temperature. At the same time the small aerosol particle volume significantly reduces the chance of efflorescence and crystallization, thus allowing for the aerosol droplets to transform into a glass upon drying. Here, the glassy samples were prepared with the MARBLES technique by atomizing dilute aqueous solutions into aerosol particles and subsequent diffusion drying. The resulting aerosol particles were collected and their phase behavior and the glass transition temperatures were investigated using DSC.

RESULTS

We will present results of the glass transition temperatures of various organics (trehalose, sucrose, citric acid, sorbitol, glycerol and 3-MBTCA) in binary mixtures with inorganic electrolytes such as sodium nitrate (NaNO₃) or ammonium bisulfate (NH₄HSO₄) (Dette and Koop, 2015). We show that NaNO₃ and NH₄HSO₄ do form glasses with different organic compounds over a wide range of mixing ratios. The corresponding Tᵥ values depend on the respective inorganic mass fraction. At very high inorganic mass fraction, efflorescence of the inorganic crystals does occur upon drying. Interestingly, in some cases, e.g. in mixtures of 3-MBTCA with NH₄HSO₄, also liquid-liquid phase separation is observed resulting in either two glassy phases or an effloresced core of the inorganic salt surrounded by a glassy organic shell. Finally, we will present results from surrogate marker compounds for isoprene SOA, and we will compare the glass formation behavior of SOA materials from different precursors such as α-pinene SOA with isoprene SOA.

CONCLUSIONS

We use the MARBLES technique recently developed in our laboratory for studying the glass formation behavior of various organic/organic and inorganic/organic aerosol particles. Our results show that inorganic salts can either effloresce or, alternatively, decrease or enhance the glass transition temperature of organics in internally mixed aerosol particles. Moreover, glass transition measurements of surrogate compounds suggest that at free tropospheric temperatures α-pinene SOA is more likely to form glassy particles than isoprene SOA.

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REFERENCES


SESSION 2:
NUCLEATION, FUNDAMENTALS

Philip Hopke: Current advances and problems in vapor-gas nucleation theory and experiments

Martin Horsh: Reexamination of the theoretical basis of Tolman’s law

Anne Maisser: Heterogeneous nucleation of n-butanol vapor on various monoatomic ions

Victor Kurasov: Nucleation in dynamic conditions at the decreasing rate of droplets growth

Barbara Hale: Reexamination of the Scaling of Homogeneous Nucleation Rates for Water

Jan Hrubý: Surface tension of ordinary water at low temperatures including supercooled region
CURRENT ADVANCES AND PROBLEMS IN VAPOR-GAS NUCLEATION THEORY AND EXPERIMENTS

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Keywords: NUCLEATION, THEORY, EXPERIMENT, ACHIEVEMENTS, PROBLEMS

INTRODUCTION

The first nucleation experiments were those of liquid and crystal supercooling by Fahrenheit (Ostwald, 1896). Nucleation of bubbles in saturated gas solutions was observed and the concept of critical embryos of the new phase was introduced during the second half of 19\textsuperscript{th} century (Volmer, 1939). The quality of vapor/liquid nucleation rate results has improved substantially beginning in the 1980s because of the development of new measurement systems (Anisimov, Hopke, \textit{et al.}, 2009). Currently, the most significant problem in nucleation is the correspondence between experimental data and theoretical predictions of nucleation rate values. Current theories are generally modifications of Classical Nucleation Theory that was completed in the 1940s. Theoretical results generally are quite reasonable for sufficiently low vapor nucleation rates where the capillary approximation is applicable (Anisimov, 2003). However, vapor-gas nucleation theory can produce values that deviate from the experimental results by several orders of magnitude (Fladerer and Strey, 2006). Experiments using different devices also show significant inconsistencies in the measured rates (for example, see Brus \textit{et al.}, 2005). The advantages and current problems of the vapor-gas nucleation experiments are discussed briefly and a view of the future studies is presented.

EMPirical METHODS

Initial measurements of vapor nucleation were made by Aitken (1888) and Coulier (1875a,b) using rapid adiabatic expansion of air saturated with water vapor to provide the necessary supersaturation. The expansion/compression cycle of Allen and Kassner (1969) was applied in the two-piston expansion chamber such as that described by Strey \textit{et al.} (1986). Supersonic jets produce the same adiabatic expansion where cluster generation and growth are decoupled (Kim \textit{et al.}, 2004). Shock tubes and supersonic jets measure high nucleation rates with values up to $10^{17}$ cm$^{-3}$s$^{-1}$ although with lower accuracy than other systems. Nucleation temperatures for adiabatic expansion techniques range from 30 to 370°K. Expansion techniques can cover nucleation rate range from $10^3$ up to $10^{17}$ cm$^{-3}$s$^{-1}$ with
measurement of five orders of magnitude in any single system. Total nucleation pressures range from approximately 100 kPa to 7 MPa.

Langsdorf (1939) created the first static diffusion chamber (SDC). The key problem is to achieve operational stability of the vapor-gas mixture in SDC with respect to convective flows. Important conditions such as “the total pressure must remain below a limiting value that depends on temperature, condensable vapor, and background gas” needs to be recognized (Heist et al., 2003). Total nucleation pressures span the interval from ~30 kPa to 4 MPa.

The flow diffusion chamber (FDC) uses a hot laminar vapor-gas flow within cold boundary conditions. An algorithm for estimation of the average nucleation rate over FDC nucleation volume was described by Anisimov et al. (1980). The maximum experimental value of the nucleation rate, \( J_{\text{max}} \), in diffusion chambers can be measured using the relationship \( J_{\text{theor}}/N_{\text{theor}}=J_{\text{max}}/N_{\text{exp}} \), where \( J_{\text{theor}} \) is maximum theoretical nucleation rate; \( N_{\text{theor}} \) and \( N_{\text{exp}} \) are the theoretical and experimental FDC particle concentrations, respectively (Hyvarinen et al., 2006; Wagner and Anisimov, 1993). The same algorithm is used for \( J_{\text{max}} \) measurements within a supersonic nozzle (Streletzky et al., 2002). FDC data from a single experimental system span six orders of magnitude in nucleation rate over a nucleation temperatures range of 230 to 400 K.

Turbulent mixing schemes are associated with wide spectrum of nucleation conditions. Turbulent flow systems are rarely used for homogeneous nucleation measurements. However, they have proved useful for heterogeneous (Lee et al., 2003; Mavliev et al., 2004) and ion-induced (Seto et al., 1997; Gamero-Castano and de la Mora, et al., 2002) nucleation studies.

The nucleation theorem (Anisimov & Cherevko, 1982; 1985; Anisimov et al., 1980; 1987; Kashchiev, 1982, etc) can be used to interpret empirical nucleation data. However, single condensable vapor-gas nucleation should be considered as binary systems because of the influence of carrier gas (CO\(_2\), SF\(_6\)) on critical embryo phase transitions (Anisimov et al., 1998, 2000).

During the past three decades, the effects of pressure and various carrier gases on homogeneous nucleation have been studied. Classical nucleation theory assumes that the carrier gas only maintains the temperature equilibrium of the clusters with the ambient media. Frank and Hertz (1956) first observed a gas-pressure effect. Gas-pressure effects are discussed by Anisimov and Vershinin (1988; 1990) who found a positive gas-pressure effect and a gas-nature effect at gas pressures from 0.10 to 0.30 MPa. They concluded (using the nucleation theorem) that carrier gas molecules were involved in the critical embryos. Heist and co-workers (1994; 1995) have reported effects of pressure and carrier gas nature on the nucleation rates for a series of short-chain alcohols. Other results have supported a dependence of the nucleation rate on the nature and total pressure of the carrier gas (Luijten and van Dongen, 1999; Luijten et al., 1999; Anisimov et al., 2000; Lihavainen and Viisanen, 2001).

Gas-pressure effects were detected by van Remoortere et al. (1996) while other measurements (i.e., Viisanen et al., 1993; Viisanen and Strey, 1994) found no carrier gas influence on nucleation rate.

Several groups made comparative measurements of nucleation rates (Anisimov et al., 1994; Wilck et al., 1998; Brus et al., 2005, etc.) The nucleation rates of n-butanol in helium using both an FDC (Hyvarinen et al., 2004) and an expansion chamber (Strey et al., 1986) show differences of 4-5 orders of magnitude. The data from the different systems can cross each other in some cases. However, the nucleation rate isotherm slopes for the two measurement systems are often very similar. The origin of these data discrepancies can be better understood through the consideration of nucleation rate surfaces (Anisimov et al., 1998; 2000).

In the most cases, the gas is treated as inert only absorbing the heat released from the phase transitions. Inconsistencies among the experimentally measured the nucleation rates from different experimental schemes are a major obstacle to better understanding of vapor-gas
nucleation. Consideration of vapor-gas nucleation as a binary system may permit the resolution of these inconsistencies. It is plausible to think that different experimental systems have the inconsistent trajectories along the nucleation rate surfaces when the vapor-gas system is treated as binary system. Several results, for example, Anisimov et al. (1998) and Anisimova et al. (2001) illustrate that high-pressure techniques are needed to study multi-channel nucleation.

To test the accuracy of experimental techniques, it is important to have a standard system that can be measured over a range of nucleation conditions. The n-pentanol–helium system was proposed in Prague in 1995 as a standard. The multiple results were collected and compared (Anisimov et al., 2000) and a reference equation was proposed for the nucleation rate of n-pentanol–helium as a practical test of measurement systems for total pressures from 0.10 to 0.30 MPa. The equation does not reproduce all of the results, but the approximation is useful to provide a relative view of the different results until a more accurate approximation can be generated. The problem of a nucleation standard can only be solved when consistent results have been independently obtained using different experimental schemes. We suggest that vapor-gas nucleation rates be represented by a surface instead of the single line that is used for most current presentations of the isothermal nucleation rate data in vapor-gas systems.

CONCLUSIONS

Accurate experimental techniques for vapor-gas nucleation research need further development. Measurable nucleation rates for the available experimental techniques span the range from 10⁻² cm⁵s⁻¹ up to 10⁷ cm⁵s⁻¹ and nucleation temperatures from ~30 K to near 1300 K. Pressures in vapor-gas systems have been achieved from 30 kPa to 10 MPa. The existing practice for vapor nucleation and the separate volumes for cluster growth should be continued to grow embryos before detection. Theory independent algorithms are needed to estimate experimental nucleation rates for the flow systems. Homogeneous nucleation rates should be measured for sufficiently high supersaturation values (Anisimov and Cherevko, 1985) when nucleation rate is over possible heterogeneous nucleation threshold. Impurities in the vapor substance must not exceed 0.2%. This level of impurities shifts the nucleation rates within one order of magnitude as shown by Anisimov et al. (1987) and Strey et al. (1995). Particle size distribution measurements are strongly recommended to identify the possibility of multiple channels in homogeneous and heterogeneous nucleation (Anisimova et al., 2001). Continuity and monotony criteria should be applied for the detection of nucleation rate surface singularities and data quality characterization (Anisimov et al. 2000). Vapor-gas systems need to be viewed as binary systems. The problem of experimental data inconsistencies should be resolved to create a nucleation standard. Uncontrolled parameter(s) need to be identified to permit consistent nucleation rate data to be derived from different methods. The introduction of one or several nucleation standard(s) is a major current problem.

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REFERENCES


REEXAMINATION OF THE THEORETICAL BASIS OF TOLMAN’S LAW

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Keywords: Surface tension, nucleation theory, thermodynamics of small systems, Tolman length.

INTRODUCTION

The surface tension of small droplets or bubbles, at the nanometre length scale, has a significant influence on the formation of dispersed phases by homogeneous nucleation (Vehkamäki, 2006). It is also crucial for understanding dispersed phase dynamics, e.g. droplet or bubble growth, decay, coalescence, and coupling between heat and mass transfer at curved interfaces (Mokshin and Galimzyanov, 2012).

Often the capillarity approximation is used: It is assumed that the surface tension \( \gamma \) of a nanodroplet is identical with the value \( \gamma_0 \) that is attained in the limit of zero curvature, i.e. infinite droplet radius, or for a macroscopic planar interface. This approximation has the advantage that \( \gamma_0 \) is usually experimentally measurable, while the actual value of \( \gamma \) is unknown for nanodispersed phases. However, the capillarity approximation leads to a paradox when the Laplace equation

\[
p'(\mu, T) - p''(\mu, T) = \frac{2\gamma}{R_{\gamma}}
\]

is applied to extremely small droplets. This equation characterizes the difference between the pressure \( p' \) in a dispersed phase (e.g. the droplet) and \( p'' \) in the surrounding phase (e.g. the vapour) in terms of the Laplace radius \( R_{\gamma} \). If \( \gamma \) is constant, then for \( R_{\gamma} \to 0 \), the pressure difference would have to become infinite. Since this is impossible, there is either a minimal value for the radius \( R_{\gamma} \), such that no droplets with a smaller radius can be in thermodynamic equilibrium, or \( \gamma \to 0 \) (and \( R_{\gamma} \to 0 \)) holds in the limit of spinodal conditions for the surrounding phase.

Most results so far appear to favour the conclusion that \( \gamma \to 0 \) for \( R_{\gamma} \to 0 \) (Malijevský and Jackson, 2012). To reflect an influence of the surface curvature \( 1/R_{\gamma} \) on the surface tension, an expansion

\[
\gamma(R_{\gamma}) = \gamma_0 + \frac{c\gamma_0}{R_{\gamma}} + O\left(\frac{1}{R_{\gamma}^2}\right),
\]

at constant temperature \( T \), can be used. If Tolman’s law (Tolman, 1949) holds, the first-order coefficient in this expansion

\[
c = -2\delta_0
\]

is obtained from the planar limit \( \delta_0 = \lim_{R_{\gamma} \to \infty} \delta \) of the Tolman length \( \delta = R_\rho - R_{\gamma} \), i.e. from the excess of the equimolar radius \( R_\rho \) over the Laplace radius \( R_{\gamma} \), which can be expressed equivalently in various related ways (Horsch et al., 2012; Tolman, 1949). In recent molecular simulation
studies, the truncation of Eq. (2) after the linear contribution in $1/R_\gamma$ has repeatedly been found to be inadequate; therefore, Tolman’s law is increasingly regarded as an unsuitable approach for quantifying the finite-size influences on $\gamma$ (Block et al., 2010; Horsch et al., 2012; Malijevský and Jackson, 2012; Werth et al., 2013; Wilhelmsen et al., 2015).

**THEORY**

In the present work, it shown that the deduction of Tolman’s law from interfacial thermodynamics relies on an inaccurate application of the Gibbs adsorption equation to dispersed phases. Hence, Tolman’s law is found to break down not only empirically and by molecular simulation (as was previously known), but also theoretically. Tolman obtained Eq. (3) by a chain of arguments based on the Gibbs adsorption equation in the form (Tolman, 1949)

$$d\gamma = -\Gamma d\mu,$$  \hspace{1cm} (4)

which relates an isothermal change in the surface tension to the adsorption $\Gamma$ and the chemical potential $\mu$ for a pure substance. For pure fluids and spherical interfaces, the adsorption and the Laplace radius are related by

$$\frac{\Gamma}{\rho' - \rho''} = \delta \left[ 1 + \frac{\delta}{R_\gamma} + \frac{\delta^2}{3R_\gamma^2} \right],$$  \hspace{1cm} (5)

where $\rho'$ and $\rho''$ are the densities of the coexisting phases. Eq. (5) is obtained by integrating over the spherical density profile. By combining this with Eq. (4) and the Gibbs-Duhem equation, the relation (Tolman, 1949)

$$\frac{d\gamma}{\gamma dR_\gamma} = \frac{[2\delta / R_\gamma^2][1 + (\delta / R_\gamma) + (\delta^2 / 3R_\gamma^2)]}{1 + [2\delta / R_\gamma^2][1 + (\delta / R_\gamma) + (\delta^2 / 3R_\gamma^2)]}$$  \hspace{1cm} (6)

is obtained, which implies the identity given by Eq. (3).

However, by reexamining this approach on the basis of the fundamental equation for the surface excess free energy (Rowlinson and Widom, 1982)

$$dA^E = \mu_dN^E - S^E dT + \gamma df,$$  \hspace{1cm} (7)

it can be shown that Eq. (4) does not take the size dependence of interfacial properties into account in a self-consistent way. Here, $f$ is the surface area, and $A^E$, $N^E$ and $S^E$ are the surface excesses of the Helmholtz free energy $A$, the number of molecules $N$, and the entropy $S$. The surface tension

$$\gamma = \left( \frac{\partial A^E}{\partial f} \right)_{N^E,T}$$  \hspace{1cm} (8)

and the specific surface excess free energy

$$\bar{\gamma} = \frac{\Omega^E}{f}$$  \hspace{1cm} (9)

are different, but related quantities, which both depend on the size of the dispersed phase. Therein, the surface excess of the grand potential $\Omega = A - \mu N$ is denoted by $\Omega^E$. A self-consistent version of the Gibbs adsorption equation, at constant temperature, is given by

$$\Gamma d\mu + d\bar{\gamma} = (\gamma - \bar{\gamma}) d\ln f.$$  \hspace{1cm} (10)

Following a reexamination of Tolman’s law and its theoretical foundations as outlined above, however, a relation between $\delta$ and the influence of the size of the dispersed phase on $\gamma$ cannot be obtained. In particular, the theoretical deduction of Eq. (6) given by Tolman breaks down, and Eq. (3) cannot be proven.
CONCLUSION

Tolman’s derivation of Eq. (6), which implies the identity \( c = -2\delta_0 \), cf. Eq. (3), is inconsistent with interfacial thermodynamics. The version of the Gibbs adsorption equation on which Tolman’s approach is based, i.e. Eq. (4), does not hold for transitions which alter the surface area, cf. Eq. (10). Since changing the radius of a droplet also changes its surface area, it is wrong to discuss the dependence of \( \gamma \) on \( R \), on the basis of Eq. (4), and Tolman’s law must be discarded.

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REFERENCES


HETEROGENEOUS NUCLEATION OF N-BUTANOL VAPOR ON VARIOUS MONOATOMIC IONS – COMPARISON OF EXPERIMENTS WITH DIFFERENT VERSIONS OF KELVIN-THOMSON THEORY

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Keywords: HETEROGENEOUS NUCLEATION, N-BUTANOL, MONOATOMIC IONS.

INTRODUCTION

The investigation of the fundamental process that enables and predicts phase change is of great interest. Both homogeneous and heterogeneous nucleation/condensation processes are applied for e.g. nanoparticle synthesis, but also are responsible for new particle formation (NPF) in the atmosphere and thus, affect our climate and human health.

With advances in aerosol instrumentation towards smaller and smaller particles an increasing attention was drawn to the investigation of the process of heterogeneous nucleation for seed particles close to the Kelvin diameter. With the introduction of the ultrafine condensation particle counter (CPC) by Stolzenburg and McMurry in 1991 particle detection down to about 3 nm became possible. For a long time the Kelvin diameter was seen as a fundamental lower detection limit for the CPCs. However, this assumption could not hold some experimental investigations. Seto et al. (1997) found that ions of about 1.5 nm could be activated in a turbulent mixing CNC (condensation nuclei counter). Gamero and de la Mora (2000) used dibutyl phthalate vapor and showed that there was no lower limit to the particle size that could be activated. The definite confirmation, that detection below the Kelvin limit is possible, was provided by observations of Winkler et al. (2008) in an expansion type CPC using monodisperse particles down to about 1 nm.

A universal theory predicting heterogeneous nucleation especially for particles smaller than the Kelvin diameter is still missing. Many seed properties that were found to have an influence on nucleation, e.g. polarity and chemical composition, are not considered in classical models such as the classical nucleation theory (CNT). The development of a theory is complicated also due to the lack of meaningful experimental measurements. Accurate experimental measurements of activation probabilities require highly homogeneous nuclei and supersaturations (Fernandez de la Mora, 2010). This still is difficult to achieve using general state-of-the-art aerosol instruments.

In this study we were able to overcome these experimental difficulties by using highly specialized aerosol instruments that can meet both of the prerequisite; firstly, a high resolution and transmission DMA for the size selection of highly monodisperse seed ions of defined chemistry and both polarities; and secondly, an expansion type CPC, exposing the seed ions to a homogeneous supersaturation. In addition to the experimental work we compared the results to existing theories by applying the classical nucleation theory (CNT) for the case of insoluble and perfectly wetting seed particles.
METHODS

Heterogeneous nucleation onto 5 different monoatomic seed ions of both polarities (K⁺, Rb⁺, Cs⁺, Br⁻, I⁻) was investigated at a nucleation temperature of 271.5K using the Size Analyzing Nuclei Counter (SANC) (Wagner et al. 2003). The ions were generated by electrospray ionization of 10 mM methanol solutions of potassium, rubidium and cesium iodide salt as well as tetraheptylammonium bromide (purchased from Sigma-Aldrich, St. Louis, MO, USA). The ions were classified by a planar differential mobility analyzer (DMA, Model P5, SEDAM Inc., Madrid, Spain). The purity of the generated ions was confirmed by DMA – Mass Spectrometry (DMA-MS), using the same planar DMA and a QSTAR XL quadrupole-time-of-flight MS, MD Sciei).

N-butanol vapor was added to the system by controlled injection from a syringe pump, followed by quantitative evaporation in a custom-made heating unit. Thereby, a well-defined and nearly saturated binary vapor-air mixture together with size selected, monodisperse ions from the DMA were passed into the temperature controlled expansion chamber of the SANC (cf. Figure 1). Vapor supersaturation was achieved by adiabatic expansion and the number concentration of droplets nucleated on the ions was measured with the Constant Angle Mie Scattering (CAMS) method (Wagner, 1985). Therewith the radius and the number concentration of the growing droplets can be determined simultaneously.

The nucleation or activation probabilities using the SANC/CAMS method can be expressed as:

\[ P = \frac{N_{\text{activated}}}{N_{\text{total}}} = 1 - \exp(-jt). \]

Here, \( j \) is the related heterogeneous nucleation rate and \( t \) is the time for activation. We define the onset conditions as the conditions at which the nucleation probability reaches the value \( P = 0.5 \).

A schematic diagram showing the experimental setup is illustrated in Figure 1. By varying the injection rate of the syringe pump and the pressure drop in the expansion chamber, different nucleation conditions were analyzed, while keeping the nucleation temperature constant at 271.5 ± 1K.

![Figure 1. Schematic diagram for the experimental setup.](image-url)
Experimental saturation ratios determined for n-butanol at constant nucleation temperature for ions with different polarity are shown in Figure 2. It can be seen in the experimental data that negatively charged ions require higher onset saturation ratios compared to positively charged ions. Furthermore the experimental results show that with increasing ionic radius also a higher $S_0$ is needed for the observed size range. This is related to the ion – dipole interaction, which scales with the inverse of the ion radius. As a consequence, it makes it harder for an already attached vapor molecule to evaporate with decreasing ion size. The nucleation probability $P(S)$ at $S_0$ has the form of a cumulative Gumbel distribution (Winkler et al. 2016)

$$P(S) = 1 - \exp\left( -\exp\left[ \ln(\ln 2) + (n^* + 1)(\ln S - \ln S_0) \right] \right).$$

By applying this form of distribution as a two-parameter fit function the parameters $n^*$ (additional number of molecules to build a critical cluster) and $S_0$ can be evaluated. Thereby the onset saturation ratio and $n^*$ can be evaluated simultaneously.

With these results we calculated the total Gibbs free energy change to form a charged n-mer from the core ion of ionic radius $r_0$ (Shannon, 1976) for the classic Kelvin-Thomson (CKT) and modified Kelvin-Thomson (MKT) equation. In contrast to CKT, the MKT equation also accounts for the change in electric potential energy of the ion due to the condensation of the dielectric film and the associated energy change due to the interaction of ions with the dipole moment of the condensing molecules (F. Yu, 2005). The corresponding ion-induced formation free energies have a minimum followed by a maximum, corresponding to a pre-nucleation cluster and critical cluster (P.M. Winkler et al. 2012). Thereby we can derive the number of n-butanol molecules in both clusters. To get the radius of the ion together with the condensed butanol molecules, we treated all ions and butanol molecules as a sphere. As a result, the measured onset saturation ratio vs. pre-nucleation and critical cluster radius can be compared to CKT and MKT.

Furthermore, previously conducted measurements for saturation ratios below 1 of the same monoatomic ions with n-butanol and the use of a vapor uptake model (V.K. Rawat et al. 2015) enable us to extrapolate the inverse mobility of the pre-nucleation cluster at a saturation ratio close to one. With these measurements and by using the approximation found by (J.M. Mäkelä et al. 1996) we were able to calculate the mobility equivalent diameter for the pre-nucleation cluster. Furthermore, by using the fit parameter $n^*$ of the Gumbel distribution or the calculated number of molecules in the critical cluster from the total Gibbs free energy we were able to calculate the geometric diameter of the critical cluster.

![Figure 2](image)

**Figure 2.** Experimental measurements of the onset saturation ratio vs. ionic radius for the observed ions.
CONCLUSION

We examined the nucleation probability of monoatomic ions upon introduction of n-butanol into the SANC. Thereby we could measure the onset saturation ratio and the additional number of n-butanol molecules to build a critical cluster by applying the Gumbel distribution. With these results and the assumption that the seed ions are spherical and perfectly wettable we were able to calculate the size of the pre-nucleation and critical cluster for different monoatomic ions of both polarities. Furthermore, by applying the vapor uptake model (V.K. Rawat et al. 2015) we were able to calculate the mobility equivalent diameter of the ions at partial pressures of n-butanol below saturation. The results agree well with predictions applying the classic Kelvin-Thomson model.

In summary, we were able to quantitatively characterize the heterogeneous nucleation process for the pre-nucleation and critical nanoclusters using monoatomic singly charged ions of both polarities as seeds. The observed behavior agrees well with predictions from the classical Kelvin-Thomson model.

ACKNOWLEDGEMENTS

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REFERENCES


NUCLEATION IN DYNAMIC CONDITIONS AT THE DECREASING RATE OF DROPLETS GROWTH

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Keywords: NUCLEATION, KINETICS.

INTRODUCTION

The most natural type of external conditions for nucleation is the situation when the external influence on the system occurs in a smooth manner. We shall consider the kinetics of the phase transformation namely under these conditions.

In the situation of dynamic conditions we can linearize the imaginary supersaturation in the absence of nucleation (i.e. the ideal supersaturation) as the function of time (or as the function of coordinate \( z \) of the amplitude of the size spectrum). The supersaturation in the absence of nucleation is simply the result of the external influence and the last notation means that we can linearize the external influence on the system during the period of intensive formation of embryos as a function of time. The possibility of such linearization is explained by the relative shortness of the period of intensive formation of embryos in comparison with other periods of the condensation process. In the situation of the slow growth the period of intensive formation of embryos will be longer than in the situation with the avalanche growth but the mentioned linearization is still possible. Then we come to

\[
G = A \int_{-\infty}^{z} (z - x)^{\alpha} \exp(bx - G) dx
\]

with the additional parameter \( b \) of the mentioned linearization. Here \( \alpha \) is the power in the law of the embryos growth. The spectrum of the embryos sizes is \( f \sim \exp(bx - G) \).

UNIVERSAL SOLUTION

The simple scaling \( z \rightarrow zA^{1/\alpha}, \quad x \rightarrow xA^{1/\alpha} \) brings equation (1) to

\[
G = \int_{-\infty}^{z} (z - x)^{\alpha} \exp(bx - G) dx
\]

and allows to cancel parameter \( A \). But it is not too simple to cancel parameter \( b \) because in the traditional approach the condition, which allows to cancel this parameter was the following: The point of decompositions has to be chosen as the maximum of the supersaturation (or as the maximum of \( f \)).

In situation with \( \alpha = 0 \) one can not satisfy this condition. Moreover, the spectrum \( f \) increases in time. The analytical solution in the case \( \alpha = 0 \) is the following

\[
f = \exp(bx - \ln(\exp(bx) + 1)) \equiv f_0
\]

One can formulate the alternative: When \( \alpha > 0 \) one can see the maximum of \( f \) and when \( \alpha = 0 \) the explicit analytical solution has been presented.
For $\alpha > 0$ one can put condition on the point of maximum. Then the standard way of derivation is possible. For $\alpha \neq 0$ we have the universal solution depended on $\alpha$. This solution satisfy the following universal equation

$$-\ln(f) + \alpha \int_{-\infty}^{0} (z-x)^{\alpha-1} f(x) dx = \int_{-\infty}^{z} (z-x)^{\alpha} f(x) dx$$

(4)

ITERATION STEPS

The main feature which has to be taken into account is the long infinite tail of the spectrum of the embryos sizes for $\alpha = 0$. The most interesting region here is the region of the rapid increase of $f$. If we choose $b = 1$ we get this region at $x \sim 0$. We can see that it is reasonable to put $b \sim 1$ for all $\alpha$. One can note an important feature: "For $\alpha > 0$ the spectrum of the embryos sizes $f$ lies lower than the spectrum $f_0$ in the case $\alpha = 0"$. Having used the property of the effective size of growth one can come to conclusion that the maximum of $f$ lies near $x = 0$ when $b = 1$. Then one can put $b = 1$ for all cases with the small values of $\alpha$.

We shall use $f_0$ as the initial approximation in the following iteration procedure

$$G_{i+1}(z) = \int_{-\infty}^{z} (z-x)^{\alpha} \exp(bx - G_i(x)) dx \quad G_0 = -\ln(f_0) + bx$$

(5)

The first iteration is

$$G_1(z) = \int_{-\infty}^{z} (z-x)^{\alpha} \left(\frac{\exp(bx)}{b} + 1\right)^{-1} \exp(bx) dx$$

(6)

To calculate $G_1$ one can use approximation

$$f_0 \equiv \frac{1}{1 + \exp(-x)} \approx f_{ap}$$

(7)

where $f_{ap} = \exp(x) - \exp(2x) + \frac{1}{2} \exp(3x)$ for $x < 0$ and $f_{ap} = 1 - \exp(-x) + \frac{1}{2} \exp(-2x)$ for $x > 0$. At $x = 0$ there is no difference between the precise result and the approximation. With the help of this approximation all integrals can be calculated in terms of the Gamma-function.

When the first approximation $G_1$ is calculated we see that the function $f_1 = \exp(x - G_1)$ which is the spectrum of the embryos sizes in the first approximation has one maximum $f_{1 \max}$ at $x_{1 \max}$. In the region $x < x_{1 \max}$ this function approximates the spectrum of the embryos sizes with a high precision. We also have $x_{\max} \approx x_{1 \max}$, where $x_{\max}$ is the coordinate of a real maximum and $f_{\max} \approx f_{1 \max}$ where $f_{\max}$ is the amplitude of the spectrum of the embryos sizes. These facts can be proven analytically.

The spectrum of the embryos sizes in the first iteration rapidly turns to zero, but the precise spectrum of the embryos sizes has a very long tail. It is necessary to correct this discrepancy. When $\alpha$ is growing then $x_{1 \max}$ goes away from $x_{\max}$: $f_{1 \max}$ goes away from $f_{\max}$ and $f_0(x_{1 \max})$ goes away from $f_{1 \max}$. But even when $\alpha = 0.5$ (this is the realistic boundary of our constructions because for $\alpha > 0.5$ one can use the decompositions starting from $\alpha = 1$) the difference between $f_0(x_{1 \max})$ and $f_{1 \max}$ is small. This allows to suggest the cut-off of the zero approximation $f_{0 \text{cut}}$ which is $f_{0 \text{cut}}(x) = f_0(x)$ for $x < x_{1 \max}$ and $f_{0 \text{cut}}(x) = f_0(x_{1 \max}) = f_{1 \max}$ for $x > x_{1 \max}$.

On the base of this initial approximation one can reproduce all constructions and get the spectrum of embryos sizes $f_1$ in the first approximation, which lies higher than the "previous first approximation".

One can analytically show that the first advanced iteration describes the form of the hill satisfactory. But there remains the long tail and it is absolutely impossible to describe this tail on the base of the iteration method because the duration of this tail is very long. Then one can propose some asymptotic methods to solve this problem.
ASYMPTOTICS

We shall construct solution for \( x \gg 1 \). It is possible to write approximately the evolution equation as

\[
G(z) = \int_0^z (z - x)^\alpha \exp(x - G(x)) \, dx
\]

(8)

instead of taking the infinite lower limit.

Now we shall use the property of effective size of growth. Since the amplitude of the spectrum of the embryos sizes is not changed too quickly one can take the size \( (z - x)^\alpha \) out of the integral and speak about the mean size \( \bar{\rho} \) of \( (z - x)^\alpha \). Then

\[
G(z) = \bar{\rho} \int_0^z \exp(x - G(x)) \, dx
\]

(9)

For \( \bar{\rho} \) one gets the following expression

\[
\bar{\rho} = \frac{\int_0^z (z - x)^\alpha \, dx}{\int_0^z \exp(x - G(x)) \, dx} = \frac{z^\alpha}{\alpha + 1} \approx z^\alpha
\]

(10)

Having differentiated \( G \) over \( z \) one has to notice that the introduced function \( \bar{\rho} = z^\alpha \) is a slow function and there is no need to differentiate it. Then

\[
\frac{dG}{dt} = z^\alpha \frac{d}{dz} \int_0^z \exp(x - G(x)) \, dx = z^\alpha \exp(z - G(z))
\]

(11)

After the integration we come to

\[
G = \ln(1 + \bar{\rho} \exp(z))
\]

(12)

with asymptotics \( G \to \ln(\bar{\rho}) + z \). This leads to the following expression for the spectrum of the embryos sizes

\[
f \sim \exp(x - G) = \exp(z - \ln(\bar{\rho}) - z) = (\bar{\rho})^{-1}
\]

(13)

and finally \( f \sim z^{-\alpha} \). Here one can introduce the arbitrary shift \( \gamma \) and the arbitrary amplitude \( \beta \). Then

\[
f \sim \frac{\beta}{(z - \gamma)^\alpha}
\]

(14)

These parameters can be determined by the requirement of the smoothness of the spectrum of the embryos sizes at the boundary between the advanced first iteration and the asymptotic. Now we shall choose this boundary.

At \( z = 0 \) the spectrum of the embryos sizes begins to grow, at \( z = z_{\text{max}} \) it attains maximum. It is reasonable to imagine the hill to be symmetric and to say that at \( z = 2z_{\text{max}} \) the hill is over. Namely at this point we can speak about the beginning of the asymptotic.

Conditions

\[
\frac{d\hat{f}_1}{dz} = -\alpha \frac{\beta}{(z - \gamma)^{\alpha + 1}} \quad \hat{f}_1 = \frac{\beta}{(z - \gamma)^\alpha}
\]

(15)

at \( z = 2z_{\text{max}} \) give the following expressions

\[
\gamma = 2z_{\text{max}} + \alpha \hat{f}_1(z_{\text{max}})/(d\hat{f}_1/dz)|_{z=z_{\text{max}}} \quad \beta = \hat{f}_1(z_{\text{max}})(z - \gamma)^\alpha
\]

(16)

The accuracy of the theory can be estimated by the error in the droplets number \( \epsilon = \frac{|N - N_{\text{ap}}|}{N} \). Here \( N \) is the precise value found from the numerical solution and \( N_{\text{ap}} \) is the number of droplets found from the presented approximation.
In consideration of the extremely long asymptotic tails we have to take care about the accurate behavior of the asymptotics. The boundary between the iteration solution and the asymptotic solution will be put in a special point \( z_{\text{bound}} \). To get \( z_{\text{bound}} \) we shall fix the beginning of the nucleation process more precise. On the base of iterations we get \( f_{\text{max}} \). Then we get the value \( f_{\text{st}} \) of the amplitude at the beginning of nucleation as

\[
 f_{\text{st}} = \frac{f_{\text{max}}}{\exp(1)}.
\]

Then we can get the coordinate \( z_{\text{st}} \) of the beginning of the nucleation process as

\[
 z_{\text{st}} = \ln(f_{\text{st}}).
\]

Then \( z_{\text{bound}} \) will be calculated according to the old recipe but with a new time of beginning of the nucleation process

\[
 z_{\text{bound}} = z_{\text{st}} + 2(z_{\text{max}} - z_{\text{st}}).
\]

One can see that even for \( \alpha = 3/2 \) the result is good even without asymptotics and even with initial approximation corresponding to \( \alpha = 0 \). For \( \alpha > 3/2 \) the result was presented earlier. All situations are considered now.

The first iteration based on \( \alpha = 1 \) in the direct iteration method gives

\[
 N_{\text{ap}} = \int_{-\infty}^{\infty} f_1(x)dx \quad f_1 = \exp(x - g_1) \quad g_1 = z - \int_{-\infty}^{z} (z - x)^{\alpha} f_0(x)
\]

and \( f_0 \) is the analytical solution corresponding to \( \alpha = 1 \).

The head of the spectrum (the amplitude, not the shape) is seriously diminished. This decrease is the main source of error. So, we need to reexamine the initial approximation.

We can scale the number \( g \) of molecules in the liquid phase to have the approximately equal amplitudes. One can calculate the constants

\[
 q(\alpha) = \int_{-\infty}^{0} \exp(-x)x^{\alpha-1}dx
\]

and instead of \( g \) consider \( g/q \) (both for current \( \alpha \) and for \( \alpha = 1 \)). This corresponds to the approximate equality of \( g(\alpha) \) and \( g(\alpha = 1) \) at \( z = 0 \). The error is seriously diminished.

One can also require the approximate equality in derivatives of \( g \) as the functions of \( x \) at \( t_\ast \) as it is considered in the balance for establishing of \( t_\ast \). Then the constants \( q \) will be

\[
 q(\alpha) = \alpha \int_{-\infty}^{0} \exp(-x)x^{\alpha-1}dx
\]

Here the values of \( q \) were calculated on the base of the ideal supersaturation, i.e. on the base of \( \exp(x) \). The results will be even better if we take \( q \) calculated on the base of solution at \( \alpha = 1 \).

All presented solutions can be improved to take into account the approximative manner of simplifications necessary for the derivation. We must mention some corrections which have to be done at the tails of the spectrum of the embryos sizes. Since the asymptotic are derived here in a simple algebraic way, one can enlarge the account of the specific features in asymptotic.

In consideration at the long tails one has to take into account the higher derivatives of the free energy of critical embryo. This account is rather simple since we know the general solution. It can be done both by the iteration approach and by the perturbation technique.

The validity of the linearization of the ideal supersaturation can be broken at the long tails. But there will be also no difficulties to correct the asymptotic for deviations from the linear case.

Details of this approach can be found in [Kurasov, 2015].

REFERENCES

REEXAMINATION OF THE SCALING OF HOMOGENEOUS
NUCLEATION RATES FOR WATER

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Technology, Rolla, MO 65409 U. S. A

Keywords: NUCLEATION, SCALING, WATER, EXPERIMENT, THEORY

INTRODUCTION

The temperature dependent scaling of the homogeneous nucleation rate, J, offers a comprehensive
comparison of rates over a range of temperature ratios, T/T_c (where T_c is the critical temperature) and
supersaturation ratios, S = P/P_0 (where P and P_0 are the ambient and equilibrium vapor pressures).
Experimental rates are often obtained via physically different background processes while the theoretical
predictions range from classical analyses to Monte Carlo (MC) and Molecular Dynamics (MD) computer
simulations with several choices of effective pair potentials. The scaling plot enables one to examine all
these data simultaneously using two parameters: Ω, the excess surface entropy per molecule (in units of k,
the Boltzmann constant) and the critical temperature for the substance or the model potential in the case of
the theoretical predictions. We examine here the scaling plot for water (Hale, 2004) and (Wyslozul and
Wölk, 2016) together with recent MD (Tanaka, 2014), (Angelil, 2015) and MC predictions at higher rates
(Hale and DiMattio, 2017). The latter higher rates place the physical process in the realm of smaller
critical cluster sizes where the discreteness of the cluster size can play a significant role and affect the
scaling exponents.

THE SCALING PLOT

In the scaling plot (Hale, 2004) -log [J/J_s] is plotted vs. the scaled free energy of formation (Hale,
1986) [16π/3] Ω^3 [T_c/T-1]^2/(lnS)^2 where J_s is a typical monomer flux factor times the monomer number
density -- often taken to be 10^26 in the cgs system of units. The excess surface entropy per molecule, Ω, is
approximately 1.5 for substances with a dipole moment and 2.0 for normal substances. The scaling plot
for the experimental and theoretical water data is shown in Fig. 1.

MC NUCLEATION RATES FOR THE TIP4P POTENTIAL MODEL
AT LARGE SUPERSATURATION RATIOS

In the interest of generating Monte Carlo simulation based nucleation rates near 10^{23} cm^3 s^{-1} the free
energy differences for small TIP4P clusters (Hale and DiMattio, 2004) at 260K, 280K and 300K (see Fig.
2) are used to predict nucleation rates at high supersaturation ratios. The results are added to Fig. 1.
Details of this process are in (Hale, 2010). The predicted nucleation rates are given in Table I.

<table>
<thead>
<tr>
<th>T/K</th>
<th>S</th>
<th>l/cm^3 s^{-1}</th>
<th>T/K</th>
<th>S</th>
<th>l/cm^3 s^{-1}</th>
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</tr>
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Fig. 1. Homogeneous nucleation rates, $J$, for water vs. the scaled free energy of formation. Much of the data in this plot was presented in Fig. 12 of (Wyslouzil and Wölk, 2016) who generously shared data files for creating the present figure which now includes data for the MD generated nucleation rates, (Tanaka et al, 2014), (Angelil et al. 2015), (Dumitrescu et al. 2017) and MC generated nucleation rates (Hale and DiMattio, 2017). See Fig. 10 of (Wyslouzil and Wölk, 2016) for remaining data sources identified at the side.

Fig 2. Helmholtz free energy differences for small TIP4P clusters scaled with $[T_c/T - 1]$ (Hale and DiMattio, 2004). The $\Delta f = \ln[Q(n)/(Q(n-1)Q(1)v_n/V)]$ where $Q(n)$ are the $n$-cluster canonical configuration integrals and $v_n$ and $V$ are the small $n$-cluster volume and system volumes respectively. The free energy differences are calculated via the Bennett technique. See (Hale, 2010) for additional formalism details.
COMMENTS AND CONCLUSIONS

For inclusion in Fig. 1 the nucleation rates in Table I were plotted vs. the scaled energy of formation using the literature reported value of the critical temperature for TIP4P, $T_c = 588$K (Vega, 2011). There was no convincing value of $T_c$ with which the free energy differences scaled in the Monte Carlo simulations. For purposes of demonstrating the scaling analysis $T_c = 588$K is used in Fig 2. It is essential to note the importance of the intercept at infinite n cluster size in Fig. 2. This intercept is equal to $\ln \left[ \frac{\text{liquid}}{\text{vapor monomer}} \right]$ and enters crucially into the determination of the n-cluster number density and subsequently the nucleation rate. Scaling does not occur unless this intercept reliably reproduces the ratio of liquid to vapor monomer number densities, with the correct temperature dependence. See (Hale, 2010) for further details.

The TIP4P data points in Fig. 1 from the present MC analysis appear to agree reasonably with the results of (Merikanto et al.2004) and surprisingly with a range of experimental data points. A feature of note is that the present TIP4P MC nucleation rates appear to have an $\Omega$ slightly larger than 1.47. At high nucleation rates the TIP4P MC data points are consistent with the MD results of (Dumitrescu et al. 2017) and not far from the MD results for the SPC/E potential (Tanaka et al, 2014) and (Angelil et al., 2015). Angelil et al. have found an exponent of 1.7 at high nucleation rates whereas the experimental data at lower rates are more aligned with the 3/2 value. This very interesting result will no doubt have important consequences in understanding the role which the effective potential model and the critical cluster size play in the scaling analysis.

REFERENCES


Hale, B. N. and DiMattio, D. J. 2017, Comments on nucleation rates at high supersaturation ratios (Unpublished).


SURFACE TENSION OF ORDINARY WATER AT LOW TEMPERATURES INCLUDING SUPERCOOLED REGION – NEW EXPERIMENTS AND MOLECULAR SIMULATIONS

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Abstract. The study presents recently measured experimental data for the surface tension of ordinary water at temperatures down to – 25 °C together with the results of the molecular simulations for the SPC/E and TIP4P/2005 force fields. The experimental data is close to the extrapolated IAPWS standard (2014) and to the correlation of Viisanen et al. (1993) commonly used in the nucleation studies. The presented experimental data and molecular simulations do not show any anomalous temperature course. An exponential growth predicted by Rogers et al. (2016) may occur at even lower temperatures.

Keywords: SURFACE TENSION, SUPERCOOLED WATER, SPC/E, TIP4P/2005

INTRODUCTION

Liquid water at low temperatures exhibits several anomalies including generally known density maximum at 4 °C, isobaric heat capacity and isothermal compressibility minima. Based on the experimental data by Hacker (1951) and some molecular simulations, e.g., Lü and Wei (2006), the surface tension of supercooled water seemed to show another anomaly – the second inflection point (SIP) in the temperature range between – 8 and + 30 °C. In this study, recent measurements for the surface tension of supercooled water down to – 25 °C are reported. In addition, new molecular dynamics simulations the SPC/E and TIP4P/2005 molecular models have been performed to study the temperature course of the surface tension.

MEASUREMENT OF SURFACE TENSION OF SUPERCOOLED WATER

Figure 1. Surface tension of supercooled water. Comparison of the new data with previous experiments, the IAPWS standard (2014), and the correlation by Viisanen et al. (1993)
Hrubý et al. (2014) and Vinš et al. (2015) obtained new experimental data for the surface tension of supercooled water. The measuring technique is based on the modified capillary rise method. The most important feature of the new apparatus is that it allows fast temperature variation and stabilization required for the measurements under the metastable conditions; more details about the design of the apparatus are provided in Vinš et al. (2013). As can be seen in Figure 1, the new data for the surface tension of supercooled water do not show any significant change in the temperature trend compared to the historical measurements by Humphreys and Mohler (1895) or Hacker (1951) and are markedly more consistent than the data by Floriano and Angell (1990).

Figure 2. Difference of the experimental data for the surface tension of supercooled water and the correlation by Viisanen et al. (1993) from the IAPWS standard (2014).

Figure 2 shows the difference of the experimental data from the IAPWS standard (2014) extrapolated below 0.01 °C. The uncertainty range of the new data is also provided. As can be seen the IAPWS standard (2014) correlates the data quite well, although a small offset occurs at temperatures below –20 °C. The correlation by Viisanen et al. (1993) provides comparable results with slightly better agreement at very low temperatures. We note that the IAPWS standard (2014) is currently being revised in order to consider also the supercooled region and to improve the uncertainty estimates (IAPWS Minutes, 2014). New verification measurements with another measuring technique using a horizontal capillary tube are being performed. Preliminary results by Vinš et al. (2016) agree with the capillary rise measurements.

MOLECULAR SIMULATIONS OF THE VAPOR-LIQUID PHASE INTERFACES OF WATER

In parallel with the experimental research, molecular dynamics simulations of the vapor-liquid phase interface have been performed. Although the simple SPC/E and TIP4P/2005 models cannot be expected to provide fully quantitative predictions for real water, we expect that the qualitative trends are the same for the real and model waters. Some preliminary results were published by Planková et al. (2014) and Vinš et al. (2015). Main motivation of the current research is to clarify the existence of the SIP anomaly. Lù and Wei (2006) applied simulation parameters by Alejandro et al. (1995) and modeled the low-temperature region using the SPC/E model. The authors claimed that the SIP anomaly, earlier indicated experimentally by Hacker (1951), was proved in their simulations.
A series of molecular dynamics simulations with two most used rigid water models SPC/E and TIP4P/2005 were conducted using a molecular dynamics package DL\_POLY [Smith & Forester (1996) and Smith et al. (2012)]. The simulations by Chen and Smith (2007) and Sakamaki et al. (2011) were considered as the main source of inspiration for the simulation settings. The vapor–liquid phase interfaces were investigated in the temperature region from −73 °C to +330 °C. Three independent runs were simulated for each temperature, except the low-temperature region where five runs were performed. An NVT ensemble with 1372 molecules and a time step of 2.0 fs was employed. The surface tension and other output properties were evaluated after the overall simulation period of 10 ns. A slab geometry was used for the simulation of the vapor-liquid interface. A liquid box was equilibrated at the desired temperature at first. Size of the initial liquid box was determined from the liquid density of the corresponding molecular model at a given temperature. Subsequently, the box was expanded by a factor of three in one direction in order to allow formation of two phase interfaces. After the expansion, the system was equilibrated for 200 ps using the Berendsen thermostat. Finally, the slab configuration was simulated for 10 ns using the Nosé-Hoover thermostat. The relaxation constant of both thermostats was set to 100 fs. The cutoffs of the Lennard–Jones interactions were set to a constant value of 14.5 Å. For electrostatic interactions direct Ewald method was used with a DL\_POLY optimization constant set to 10^{-5}. The new results agree with other simulations from the literature depicted in Figure 3. Both water models show the same slope as the IAPWS correlation, the TIP4P/2005 agree with the experimental data quantitatively better. The SIP anomaly observed in the simulations by Lü and Wei (2006) could not be proved.

**CONCLUSIONS**

The surface tension of supercooled water has been investigated both experimentally by molecular simulations. Recent experimental data (Hrubý et al., 2014; Vinš et al., 2015) down to −25 °C do not show the previously reported anomaly (Hacker, 1951) in the temperature trend and can relatively well be reproduced both by the IAPWS standard (2014) extrapolated below 0.01 °C and the correlation by Viisanen et al. (1993). The molecular simulations performed with the SPC/E and TIP4P/2005 molecular models for water with special focus on the low-temperature region are in qualitative agreement with the experiments as they do not show any anomaly in the surface tension either. However, recent simulations by Rogers et al. (2016) with a more sophisticated WAIL force field (Pinnick et al. 2012) indicated a clear
exponential growth at very low temperatures which might be related to a subtle deviation of our experimental data from the extrapolated IAPWS standard which is visible in Figure 2.

ACKNOWLEDGEMENTS

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REFERENCES

Hacker, P.T. (1951) Experimental values of the surface tension of supercooled water, NACA TN 2510.
IAPWS revised release on surface tension of ordinary water substance (2014) http://www.iapws.org
SESSION 3: 
AEROSOLS IN THE TROPOSPHERE

Josef Dommen: From new particle formation to CCN at the high altitude station Jungfraujoch: an overview

Federico Bianchi: The Himalayan aerosol factory: the chemistry of new particle formation

Johannes Schneider: Secondary organic aerosol formation in tropical upper troposphere

Stephany B. Mazon: Nucleation mode ions and particles in the Amazon: inside vs. outside canopy conditions

Indra Chandra: Current situation of atmospheric nanoparticles in Fukue Island, Japan

Laura Riuttanen: Observational evidence for aerosols increasing upper tropospheric humidity
INTRODUCTION

To quantify how anthropogenic emissions alter global clouds and climate it is essential to understand the global budget of cloud condensation nuclei in present time as well as in the past. Merikanto et al. (2009) estimated that 45% of global low-level cloud condensation nuclei (CCN) are derived from nucleation, with the remainder stemming from primary emissions. In their model new particle formation (NPF) was parameterized by a binary homogeneous nucleation scheme of sulfuric acid and water in the free troposphere and by a cluster activation scheme for the boundary. The latter is based on the observation that in the planetary boundary layer (PBL) nucleation rates are often proportional to the sulfuric acid concentration, whereby the nucleation rate coefficient is derived empirically. Only recently, laboratory experiments provided reliable nucleation rates of various chemical systems for atmospheric conditions in terms of trace gas concentrations and temperature. At temperatures and sulfuric acid concentrations occurring in the PBL homogeneous nucleation of pure sulfuric acid-water is not feasible (Kirkby et al., 2011). It requires additional molecules like ammonia, amines and oxidized organics to form stable clusters with sulfuric acid, which then can grow to larger particles (Kirkby et al., 2011; Almeida et al., 2013; Riccobono et al., 2014; Zhang et al., 2004). Kirkby et al. (2016) could even show that highly oxygenated molecules (HOMs), which were formed through the oxidation of the monoterpene D-pinene, nucleated without sulfuric acid. However, it is not yet known to what extent these nucleation mechanisms, i.e., sulfuric acid with stabilizing gases and pure organic nucleation, contribute to PBL and free troposphere nucleation, respectively. Dunne et al. (2016) implemented parameterizations of the ternary nucleation measurements from the CLOUD project into a model. They found that almost all new particle formation over the entire troposphere involves NH$_3$ or organic compounds. Pure biogenic nucleation was also estimated from global model simulations to increase CCN in the present day and even more in the preindustrial atmosphere (Gordon et al., 2016).

Reports on ambient nucleation events are mostly restricted to nucleation and growth rates. Correlations with sulfuric acid have been found but information on the chemical composition of nucleating clusters is very scarce. Sulfuric acid-amine clusters containing four H$_2$SO$_4$ molecules and one amine molecule could be measured by Zhao et al. [2011] and ammonium salts were observed in the 8-20 nm particle size range during field measurements by Smith et al. [2010]. At the forest station Hyttiälä HOMs have been identified as possible precursors of nucleation (Kulmala et al., 2013). In coastal regions iodine oxoacids and iodine oxide vapors have been identified in growing clusters during nucleation events (Sipilä et al., 2016).

Here we present measurements from the High Altitude Research Station Jungfraujoch (Switzerland), which is located above 3500 m a.s.l. in the center of Europe. It is thus an ideal place to study free tropospheric conditions, which are temporarily influenced by PBL air to various degrees. We report on the size distribution of aerosols, their concentration and the source of CCN from long-term monitoring.
Furthermore, from extended measurement campaigns nucleation and growth rates were determined and the chemical composition of gases and clusters during nucleation events was identified.

**METHODS**

The high altitude research station Jungfraujoch (http://www.ifjungo.ch/jungfraujoch/) is located in the middle of the Swiss Alps (7° 59' 2" E, 46° 32' 53" N). This station is part of the Global Atmosphere Watch (GAW) program and the Swiss National Air Pollution Monitoring Network (NABEL). The aerosol measurements, which have contributed to the GAW program since 1995 are described in Bukowiecki et al. (2016). A sequence of condensation particle counters (CPC) has been in operation since 1995 and a scanning mobility particle sizer (SMPS) since 2008. The data from these instruments has been used to create a climatology of nucleation events. During a long campaign taking place from January 2013 until May 2014 an atmospheric pressure interface-time of flight mass spectrometer (API-TOF; run in negative mode), a nano-SMPS and a CPC with a cut-off of 3.2 nm were operated in addition to the above-mentioned long-term instrumentation. Moreover, two intensive campaigns with additional instrumentation were performed in January/February 2013 and February/March 2014, each of them of approximately 1 month duration. Details of all instrumentation are given in Table 1.

<table>
<thead>
<tr>
<th>Instrument</th>
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<th>Intensive</th>
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<tr>
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</tr>
</tbody>
</table>

Table 1. Overview of instrumentation at the Jungfraujoch and their installation period. CI-API-TOF = Chemical Ionization Atmospheric Pressure interface-Time of Flight mass spectrometer.

**CONCLUSIONS**

The size distribution measured between 20 and 600 nm in diameter was found to be typically bimodal with relatively stable mode diameters and widths throughout the year (Herrmann et al., 2015). Days were classified as non-nucleation days, in-situ, off-site and unclassified nucleation events. NPF events were further divided into several sub-types. Overall, an NPF event frequency of 14-20% was found with no clear seasonal dependency (Herrmann et al., 2015; Tröstl et al., 2016). Nucleation rates at 3.2 nm ranged from 0.2 to 7.5 cm\(^{-3}\)s\(^{-1}\) and growth rates from 0.9 to 12 nm h\(^{-1}\) in the size range 5-15 nm (Tröstl et al.,...
2016). Freshly nucleated particles do not directly grow to CCN size but grow in steps over several days. From the chemical point of view nucleation events can be divided into two classes. In the less abundant class cluster formation is dominated by sulfuric acid –NH₃ adducts. Figure 1 shows the time evolution of sulfuric acid-ammonia clusters measured with the API-TOF during such a nucleation event which occurred on 02 March 2014 (Bianchi et al. 2016). A nucleation rate of $J_{12} = 4.8 \text{ cm}^{-3}\text{s}^{-1}$ and a growth rate of $4.8 \text{ nm h}^{-1}$ between 5-15 nm were measured on that day.

![Figure 1](image1.png)

**Figure 1.** Time evolution of sulfuric acid-ammonia clusters measured with the APi-TOF during the nucleation event on March 02, 2014. The legend shows the number of sulfuric acid molecules that are present in the clusters along with the number of ammonia molecules, $n$ ($n < \text{number of } \text{H}_2\text{SO}_4$).

![Figure 2](image2.png)

**Figure 2.** Mass defect plot from API-TOF measurements during a nucleation event dominated by HOMs. Black dots indicate identified compounds, grey circles are unidentified compounds.
The dominant fraction of nucleation events was driven by condensation of highly oxygenated molecules. A clear increase of these compounds was observed in the API-TOF as well as in the CI-APiTOF (Bianchi et al., 2016; Frege et al., 2016) as seen in Figure 2. An analysis of the mass spectra allowed us to identify different types of HOMs, which may be attributed to different sources.

ACKNOWLEDGEMENTS

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REFERENCES

THE HIMALAYAN AEROSOL FACTORY: THE CHEMISTRY OF NEW PARTICLE FORMATION

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Keywords: Nucleation, Free Troposphere, Mass Spectrometry, Ions.

INTRODUCTION

A significant fraction (> 50%) of cloud condensation nuclei (CCN) in the atmosphere arises from new particle formation (NPF) (Merikanto et al., 2009) where 35% are directly formed in the free troposphere (Merikanto et al., 2009). While NPF has been observed in many places around the world, the mechanisms governing this process are still poorly understood and subject to on-going research. One of the main goals is to elucidate the factors and underlying mechanisms governing the initial formation of molecular clusters and particles smaller than 2 nm diameter from vapours in the free troposphere. For example, many of the compounds participating to NPF remain still unknown. The only compound that certainly plays a major role is sulfuric acid (H₂SO₄) (Kirkby et al., 2011). Together with ubiquitous water vapour (H₂O), H₂SO₄ is believed to be the main source of new particles in the middle and upper troposphere. However, no study has hitherto confirmed this hypothesis. So far, most NPF measurements have been performed in either the planetary boundary layer or by airplane. Within the relatively warm boundary layer, H₂SO₄ alone cannot explain neither the NPF rate nor the subsequent growth rate (Kirkby et al., 2011). Other compounds are thus required to contribute to NPF by stabilizing H₂SO₄ molecules during the initial cluster formation.

Laboratory experiments and quantum chemical calculations have identified potential candidates that may play a role in stabilizing the initially formed clusters, such as ions (Kirkby et al., 2011), ammonia (NH₃) (Kirkby et al., 2011, Kürten et al., 2016, Bianchi et al., 2012), amines (Almeida et al., 2013; Bianchi et al., 2014), and possibly a wide range of oxygenated organic molecules (Riccobono et al., 2014). In addition to that, recent studies have shown that NPF involving only highly oxidised molecules (HOMs), without sulphuric acid, is possible (Bianchi et al., 2016; Kirkby et al., 2016; Tröstl et al., 2016).

Until now, only a few studies have observed NPF at high altitudes (Garcia et al., 2014; Rose et al., 2015; Venzac et al., 2008). These measurements have shown that NPF can frequently take place at high altitudes. The mountain ridges can represent a source of particles from planetary boundary layer (PBL) to the free troposphere, through the valley breeze system, and the observed frequency of NPF at high altitude is generally high. However, none of these have identified the chemical composition of the growing clusters, and only a few have managed to measure particles or ions down to 1 nm in size by using, for example, a Neutral cluster Air Ion Spectrometer (NAIS). Therefore, while these studies confirm that NPF at high altitude is important to study, they are insufficient for a reasonable evaluation of the underlying mechanisms which serve to improve the accuracy of NPF representation in models. A detailed
framework that unifies the particles “physical properties and the vapours” chemical composition is required to understand from first principles the fundamental pathways by which NPF occurs in the atmosphere. Recent instrumental advances, like the Atmospheric Pressure interface Time-Of-Flight (APiTOF) mass spectrometer, present a unique opportunity to determine the chemical ingredients responsible for NPF and cluster growth in the free troposphere.

In the last few years, we have focused our studies on further characterizing NPF processes at high altitudes taking these new mass spectrometers in order to have a better understanding on the chemical cluster composition and therefore the nucleation precursors. Our first measurements were performed at the Jungfraujoch station (Switzerland) and have been described in recent publications (Bianchi et al., 2016, Trostl et al., 2016b, Frege et al., 2017). More recently, we have conducted a similar experiment at the Nepal Climate Observatory Pyramid (NCO-P) above 5000 m, close to the Everest Base Camp. Here we present results from the latest campaign with a special focus on the mechanism driving NPF at a high altitude in the Himalayan region.

METHODS

In November and December 2014, we conducted measurements with state-of-the-art instrumentation, including APiTOF, Particle Size Magnifier (PSM) and NAIS, at the Himalayan Nepal Climate Observatory Pyramid (NCO-P, 5079 meters asl) situated on the southern slope of the Himalayas, in the remote Khumbu Valley, on the top of the hill above the International Pyramid Laboratory. A picture of the measurement site is shown in Figure 1.

![Figure 1. The Nepal Climate Observatory Pyramid (NCO-P) station, situated at 5079 m asl, about 100 m above the Pyramid Laboratory.](image)

In order to measure the chemical composition of the neutral clusters we used a nitrate based Chemical Ionization Atmospheric Pressure interface Time-Of-Flight (CI-APi-TOF) mass spectrometer. The same instrument, without the chemical ionization source, (APi-TOF) allowed us to also measure the naturally charged ions (positive and negative). Using a NAIS we quantified the particle and ion number size distributions and finally with the PSM we were able to determine the particle number concentration ($D >1 \text{ nm}$) which we then used to calculate the growth rates between 1 and 2.3 nm. The station is also permanently equipped with a Scanning Mobility Particle Sizer (SMPS). Besides this set of instruments specifically for the observation of NPF events, other parameters like ozone and sulphur dioxide concentrations were continuously monitored at the NCO-P station.
RESULTS

The location selected for this study, is different from the previous studied on in the Alps (Bianchi et al., 2016, Tröster et al., 2016b). For instance, while the Jungfraujoch station is located on top of a mountain, the NCO-P station is situated at the end of the Khumbu valley, hough at an altitude above 5000 m. The main process driving the variability of the atmospheric pollutants at NCO-P is the alternation of valley and mountain breeze that can be superposed to long-range transport events. For the first time, an API-TOF was deployed at such a high altitude (i.e. 5079 meters a.s.l.).

During the measurement period (23 days of good measurements), we observed and characterized 18 NPF events at the NCO-P station. NPF were characterized from the combined PSM, NAIS and SMPS measurements within a size range from 1.1 nm to 80 nm. All NPF events occurred during clear-sky conditions, and they were observed right after the onset of wind coming up from the valley. Figure 2 confirms the ion size ion distribution found in a previous study (Venzac et al., 2008) and, for the first time, we were able to follow the growth of neutral cluster from 1.1 nm (with the PSM) up to 42 nm (with the NAIS). Figure 2 also shows that every nucleation event is observed in the ion mode and as well as in the neutral clusters. Since the ions are limited by the ion production rate the neutral clusters concentration was 1-2 order of magnitude higher than the ion concentration.

![Figure 2](image-url)

**Figure 2.** Several nucleation events observed with NAIS and PSM at NCO-P, Nepal, 5079 m asl. The top two panels present the ion size distribution from 0.8 nm up to 42 nm. The bottom panel shows the neutral cluster size distribution measured with the PSM (from 1.1 to 2 nm) and with the NAIS from (2 to 42 nm).

Depending on the day, we operated the API-TOF in negative or positive mode to measure the chemical composition of the respective ions. When equipped with a nitrate based chemical ionization unit (Cl-API-TOF) we were also able to detect neutral compounds like sulphuric acid and HOMs. We changed the measurement settings in order to have a similar number of days/events measured with each of the three modes. Thanks to this approach we were able, for the first time, to determine the chemical composition of the growing clusters in such location.

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REFERENCES


Secondary organic aerosol formation in tropical upper troposphere

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Keywords: Aerosol Mass Spectrometry, Airborne Measurements, Secondary Organic Aerosol, IEPOX-SOA.

INTRODUCTION

The HALO aircraft campaign ACRIDICON-CHUVA (Aerosol, Cloud, Precipitation, and Radiation Interactions and Dynamics of Convective Cloud Systems) aimed to better understand and quantify aerosol-cloud-interactions and radiative effects of convective clouds (Wendisch et al., 2016). HALO is the German High Altitude and Long Range Research Aircraft. The campaign was conducted in September and October 2014 in Manaus, Brazil, during the transition time between dry and wet season.

Flight altitudes range between the boundary layer (∼ 2 km) and the upper troposphere (∼ 15 km). Because of the pristine forested region in the Amazon, it is expected that the main fraction of the aerosol chemical composition is organic (Martin et al., 2009; Chen et al., 2009; Pöschl et al., 2010; Schneider et al., 2011).

Volatile organic compounds (VOCs) are emitted by the forest, and through atmospheric oxidation and chemical processes secondary organic aerosol (SOA) can be formed (Zhang et al., 2007; Jimenez et al., 2009). One important VOC is isoprene (C5H8, 2-methyl-1,3-butadiene), which is mainly emitted by the Amazon tropical forest (Guenther et al., 2012). Photooxidation and further reactions under certain background conditions can lead to isoprene epoxydiols (IEPOX), which can be reactively taken up by particles and, thus, secondary organic aerosol derived from IEPOX (IEPOX-SOA) can be formed (Carlton et al., 2009; Surratt et al., 2010). Several field studies for investigating IEPOX-SOA were conducted in different regions (Hu et al., 2015). During a recent aircraft study in the Amazon rain forest the highest concentrations of IEPOX-SOA were measured at the top of the boundary layer with a maximum flight altitude of 5 km (Allan et al., 2014). Here we want to present aerosol chemical composition measurements and focus on IEPOX-SOA at different altitudes from the ACRIDICON-CHUVA campaign.

METHODS

During the ACRIDICON-CHUVA campaign we operated a Compact Time-of-Flight Aerosol Mass Spectrometer (C-ToF-AMS) (Drewnick et al., 2005) to investigate aerosol and cloud residual composition in and around deep convective systems. The C-ToF-AMS was connected to two different inlets: the HALO Aerosol Submicrometer Inlet (HASI) samples aerosol particles, whereas the HALO Counterflow Virtual Impactor (HALO-CVI) samples cloud droplets and ice particles during
in-cloud measurements so that cloud residual particles can be analyzed (Ogren et al., 1985). The size range of the C-ToF-AMS is between 40 nm and 800 nm and the time resolution is 30 s. Dependent on the equivalent potential temperature the vertical profiles of the mass concentrations are divided into three regimes: boundary layer (0 - 2 km), free troposphere (2 - 8 km) and upper troposphere (8 - 15 km). Here we want to focus on background aerosol data which are measured outside of clouds.

RESULTS AND DISCUSSION

The main fraction of the background aerosol consists of organics, as expected. Mean aerosol mass concentrations are 3.4 µg/m³ for organics, 0.2 µg/m³ for nitrate and 0.6 µg/m³ for sulfate, with maximum concentrations of 28.9 µg/m³ for organics, 2.1 µg/m³ for nitrate and 9.1 µg/m³ for sulfate. Especially the high organic mass concentrations were not anticipated. These numbers are mean and maximum values over all altitudes, respectively.

Figure 1 shows vertical profiles of the three species organics (green), nitrate (blue) and sulfate (red). Maximum values of all three species are at lower altitudes between 0 km and 5 km, including the boundary layer, which has its maximum height around 2 km altitude for most of the flights. At middle altitudes (5 km to 8 km) mass concentrations of all three species decrease. Mass concentrations in the upper troposphere (8 km to 15 km) show a behaviour which is not expected as such. Organics as well as nitrate aerosol mass concentrations increase again, whereas sulfate mass concentration does not change in comparison to concentrations at middle altitudes.

From further analysis of the organic mass spectra, we identified IEPOX-SOA at all altitudes. Measured values confirm literature background values (Hu et al., 2015) for the boundary layer. Interestingly, at the upper troposphere IEPOX-SOA fraction is increasing. Either vertical transport of boundary layer particles or formation of IEPOX-SOA during the transport and/or in the upper troposphere can explain this observation. It is also possible to use C-ToF-AMS data to determine the aging (oxidation state) of organic aerosol. Especially in the upper troposphere less aged organics that did not experience much photooxidation are observed, in contrast to the boundary layer, where aged organics are dominant. Those less aged organics are also related to IEPOX-SOA. Thus we conclude that after isoprene is emitted, atmospheric processing of this gaseous precursor happens during vertical transport and finally the reactive uptake onto pre-existing particles occurs in the upper troposphere (Schulz et al., 2017, in prep.).
ACKNOWLEDGEMENTS

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REFERENCES


NUCLEATION MODE IONS AND PARTICLES IN THE AMAZON: INSIDE VS. OUTSIDE CANOPY CONDITIONS

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Keywords: Amazon, ions, rain events, new particle formation

INTRODUCTION

New particle formation (NPF) has been observed all across the world (Kulmala et al. 2004; Manninen et al. 2010), under all ecosystems, both on land and over ocean, and from sea level to the free troposphere. The climatic relevance of NPF in contributing to total atmospheric particle loading makes it a necessity to quantify this process accurately in order to improve climate model predictions at a global scale (Jokinen et al. 2015). The Amazon basin, the largest rainforest on Earth, plays an important role in the distribution of water, energy, and particulate matter not only at a regional level, but globally (Martin et al. 2016, 2017). However, NPF have not been observed on ground level in the Amazon rainforest. Zhou et al. (2002) and Wang et al. (2016) have reported nucleation mode particles likely formed at cloud outflows in the free troposphere and subsequently transported and observed at ground level via downdrafts, but no NPF has been observed to begin at ground level. In this study, we characterize nucleation mode ions and neutral particles in the size range of 0.8 nm to 20 nm in the northern Amazon Basin. We compare inside canopy (ZF2) versus clearing site (T3) concentrations and seasonality of small and intermediate ions and total particles. Our data includes long-term measurements from the ZF2 site (Dec. 2011 to Jan. 2014) and two intensive observational periods (IOPs) for T3 site, covering the dry and wet seasons. We observed and enhanced production of small and intermediate ions during periods of rain at ZF2 site, which we refer to as ‘rain events’. Rain events are likely ions generated from the splashing of rain droplets (balloelectic effect). At clearing site T3, rain did coincide with ion bursts but we did not observe as high concentrations or duration of ions as during the rain events in ZF2. Additionally, we present for the first time to the authors’ knowledge NPF events beginning at ground level at the T3 clearing site.

METHODS

This study compares ions and total particles concentrations inside the 30-m high rainforest canopy (ZF2) and at a clearing site (T3) within the Amazon Basin. Site ZF2 includes measurements from December 2011 to January 2014, 60 km north of Manaus, Brasil (−2.6098, −60.2092W). Site T3 is a clearing 70 km downwind of Manaus, near Manacapuru, (−3.2133S −60.5987W). Measurements at this site were conducted in comination with the ARM Mobile Facility during two IOPs, conducted from Feb–Mar and Sep–Oct 2014 for the wet and dry season, respectively. The same ion spectrometer (NAIS, Manninen et al. 2016) with a detection range of 0.8–40 nm ions diameter, was used first in the ZF2 site and subsequently taken to the T3 site. Additionally, ZF2 site included meteorology data (such as temperature, wind direction and speed, rain intensity) and a DMPS (differential mobility particle sizer; Backman et al., 2012) instrument placed at ground level but with an inlet raised 60 m above the ground to measure particle number size distribution of 6–800 nm mobility diameters. Site T3 aerosol data includes an ultrafine
condensation particle counter (uCPC) and a particle size magnifier (PSM) to detect sub-3 nm aerosol particles.

Figure 1. An example of (B) a rain event inside canopy at site ZF2 on 12-Feb-2013. Concentration of negative 2–4 nm and 4–20 nm ions increases (C) with the onset of rain (D). The NAIS ion surface plot (B) shows intermediate ions lingering at 15:00 local time when no rain is recorded. Meteorology data include wind speed (WS; D), wind direction (WDIR) and temperature (Temp; E). A DMPS surface plot shows indications of a NPF event occurring at 60 m above canopy level

RESULTS AND CONCLUSIONS
The early morning development of the boundary layer can be seen in the ion diurnal at the clearing site T3. Inside-canopy site ZF2, on the hand, shows a steadier concentration of 0.8–4 nm throughout the day and night hours, likely an effect from the canopy itself which could balance ion sources and sinks and prevent the deep, diurnal convection present at the clearing site. Additionally, two types of events were identified as particular to each site: site ZF2 presented bursts in ion concentration for small and intermediate size ions, which lasted at least as long as the rain (Figure 1). No NPF events where observed on ground level at this site. However, the DMPS data resulted in 2 possible NPF events occurring at above canopy level (60 m from the ground) while the NAIS directly below only registered the rain event (Figure 1A). NPF events were observed, for the first time at ground level, only in Site T3.

Rain-events at site ZF2 showed a linear correlation between the ion concentration and the intensity of the rain suggesting that the ions are a result of charged rainwater droplets breaking off. However, during some rain events we observed elevated concentrations of ions lasting longer than the duration of the rain shower. The NAIS instrument did not show signs of electrometer over-saturation which could explain a false ion detection. Furthermore, the same instrument did not observe rain events as strong and as long-lasting when
it was measuring at the clearing site T3. Site T3 data resulted in 8 days with NPF events observed in ion and particle surface plots.

ACKNOWLEDGEMENTS

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REFERENCES


CURRENT SITUATION OF ATMOSPHERIC NANOPARTICLES IN FUKUE ISLAND, JAPAN

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Keywords: New particle formation, growth, aerosol, long-range transport, East Asia.

INTRODUCTION

Various sources of air pollution, for example, from the coal-fired power plant, cement industry, crematories, and the other anthropogenic emissions particularly in the East Asia were influenced the air quality not only in the local area but also in the other region. These emissions such as SO2, NOx, Volatile Organic Compounds (VOCs), and particulate matter (PM) as well as meteorological conditions have been contributing to the more severe air pollution. Xue et al. (2016a) reported that winter season is the highest emissions of air pollutants in Beijing, China, due to the increased indoor heating demand. They also reported that SO2 concentration is one of primary emissions into the atmosphere. Such a trend probably will be increased if the local government used business-as-usual scenario rather than improved pollution control schemes (Xue et al., 2016b and 2016c). Therefore, for instance, these pollutants are transported over a long distance by westerlies and raise serious problems in the downstream regions. They indirectly affect the regional size distribution through a process of secondary particle formation, also known as new particle formation (NPF). Furthermore, the fresh atmospheric aerosol was growth to several tens nanometers by further condensation and coagulation of low volatility and semi-volatile vapors, and heterogeneous reactions (Young et al., 2013).

We conducted field observation to investigate NPF and growth events on the ground based station in Fukue Island, Japan over five periods (Feb. 23 to Mar. 7, 2013; Nov. 7 to 20, 2013; Nov. 2 to 24, 2014; Feb. 27 to Mar. 17, 2015; and Feb. 27 to Mar. 25, 2016). Various instruments were carried out to this site, such as mobility size distributions, gaseous concentrations, PM2.5 mass concentration, aerosol chemical components, and meteorological parameters. A several NPF with onset diameters as small as 5 nm and followed by the successive growth of particles to mobility diameters of several tens nanometers were identified and associated with the long-range transport of polluted air masses from the East Asian region (Chandra et al., 2016). The daily average of PM2.5 concentration was typically less than 20 μg·m⁻³, but sometimes the value exceeded the target of environmental standards (≤35 μg·m⁻³ in daily average; Wakamatsu et al., 2013). The concentration of SO2 during an observation campaign was 2.3±2.2 ppb, 1.3±1.1 ppb, 1.0±0.5 ppb, 1.4±1.0 ppb, and 0.8±0.5 ppb respectively. However, we only identified three days event over the 28-days observation period in 2016 (~10%). This situation was in contrast to the events in 2013 when we identified around 60% of event days. The level concentration of SO2 and PM2.5 might be influenced the formation rate of newly-formed nanoparticles in Fukue Island, Japan. In the present study we measured mobility size distribution using 1nm-Scanning Mobility Particle Sizer (SMPS) ranging from 1 to 30 nm. We analyzed how the concentration of the possible precursor (SO2) and mass concentrations of PM2.5 of atmospheric aerosol, as well as meteorological conditions, influenced the condition of the NPF.
METHODS

We conducted a field study to investigate NPF and growth events under the influence of air pollution transported over large distances in the East Asia region as part of the Impacts of Aerosols in East Asia on Plants and Human Health (ASEPH) project. We selected Fukue Island (32.8°N, 128.7°E), a rural island located in the outflow region of the East-Asian plume, as a supersite for field observation. In the first study, 2012, we collected time-resolved data on the mobility size distribution and number concentration by a long-SMPS with a size range of 14-670 nm (Seto et al., 2013). We added a Nano-SMPS to measure mobility size distribution between 2.5 nm and 64 nm over 2013-2015 period, and it was replaced by a 1nm-SMPS ($D_n > 1$ nm) in 2016. The measurements of the concentrations and chemical composition of atmospheric aerosols and gases were available from the observation system of National Institute for Environmental Studies (NIES) and various meteorological data were available from the observation network for aerosol-cloud-radiation interaction (SKYNET).

RESULTS AND DISCUSSION

Figure 1 shows the daily-averaged SO$_2$ concentration against PM$_{2.5}$ mass concentration. We plotted the data over the winter (Feb. 23 to Mar. 7, 2013; Feb. 27 to Mar. 17, 2015; and Feb. 27 to Mar. 25, 2016) and autumn (Nov. 7 to 20, 2013; and Nov. 2 to 24, 2014) campaign. As clearly seen, SO$_2$ and PM$_{2.5}$ concentration in 2016 was slightly smaller than the level concentrations in 2013. This variation was close to the data from Goto station (32.75°N, 128.68°E), which measured by Ministry of the Environment, Japan (http://nagasaki-taiki.aao.netvolante.jp/graph/monthly). Kurokawa et al. (2013) reported that the emission of SO$_2$ in China was decreased since 2007 due to local government have been controlling the emission gas through desulphurization technologies in the large power plants. The SO$_2$ are well-known as one of the main precursor gas in the daytime atmospheric NPF through photochemical processes (Birmili and Wiedensohler, 2000; Yu, 2010). Therefore, the decline of SO$_2$ concentration might be influenced the NPF events and growth in Fukue Island, Japan.

![Figure 1. The daily-averaged SO$_2$ concentration against the PM$_{2.5}$ mass concentration.](image-url)
Figure 2. Diurnal variation of atmospheric species and meteorological data on Mar. 10, 2016: (a) particle size distributions ($1 < D_p < 600$ nm), (b) particle number concentration ($1 < D_p < 600$ nm) and SO$_2$ concentration, (c) PM$_{2.5}$ concentration and mass concentration of chemical components (Cl$^-$, NO$_3^-$, SO$_2^{2-}$, Org, and NH$_4^+$), (d) meteorological data (Pressure ($P$), Solar radiation ($I$), Temperature ($T$), and Relative humidity ($RH$)), (e) daily weather map provided by Japan Meteorological Agency and 48-h back trajectory calculated by NOAA HYSPLIT model, and (f) vertical direction of air mass by the trajectory analysis.

Figure 2 shows pick-up data on the time variation of atmospheric species and meteorological data (Mar. 10, 2016). A remarkable increase in the concentration ($dN/dlogD_p > 10^4$ cm$^{-3}$) of nanoparticles ($D_p < 30$ nm) was detected around 13:00 and continued until early evening under high concentration of the Aitken mode particles (~100 nm). The relatively high concentration of SO$_2$ (>1 ppb) and PM$_{2.5}$ (>10 $\mu$g·m$^{-3}$) were identified before the nucleation period. It suggests that the level concentration of SO$_2$ was sufficient to generate new particles under gradually decrease of PM$_{2.5}$ mass concentration. This variation in the SO$_2$ and PM$_{2.5}$ concentrations have a similar pattern with the fluctuation of the particle mass concentrations measured by ACSM (PM$_1$). The chemical species of these particulate matter (PM$_1$) are dominated by nitrates as well as sulfates and organics before an event period.

As shown in Fig. 2 (d), the event day was identified under cloudy day with a relatively high level of relative humidity (>60%). It seems that some typical delay of nucleation time due to the insufficient amount of solar radiation. Based on the NOAA HYSPLIT model (Draxler and Rolph, 2013), two air masses origin were coming from the north and northwest of China by northwesterly wind under low pressure (~1010 hPa) at Fukue site. It suggest that the transboundary transport of air pollutions were observed and associated with the NPF event in the down-flow region.

CONCLUSION

Field observations to investigate the atmospheric new particle formation (NPF) and growth events were carried out on the outflow region of the East-Asian plume in the East-China Sea (Fukue Island, 32.8°N, 128.7°E) over five periods (Feb. 23-Mar. 7, 2013; Nov. 7-20, 2013; Nov. 2-24, 2014; Feb. 27-Mar. 17, 2015; and Feb. 27-Mar. 25, 2016). The daily-averaged SO$_2$ concentration and PM$_{2.5}$ concentration are 2.3±2.2 ppb and 17.6±8.5 $\mu$g·m$^{-3}$, 1.3±1.1 ppb and 16.7±10.6 $\mu$g·m$^{-3}$, 1±0.5 ppb and 14.9±6 $\mu$g·m$^{-3}$, 1.4±1 ppb and 13.8±4.7 $\mu$g·m$^{-3}$, and 0.8±0.5 ppb and 14.7±5.3 $\mu$g·m$^{-3}$ respectively. The
scattering plot between SO$_2$ and PM$_{2.5}$ concentration tends to be decreased from year-to-year. It was influenced the new particle formation (NPF) and growth events in 2016 campaign when we only identified the less number of event days (~10%). Therefore, the NPF events were influenced by the transboundary transport of polluted air under certain meteorological conditions.

ACKNOWLEDGEMENTS

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REFERENCES


OBSERVATIONAL EVIDENCE FOR AEROSOLS INCREASING UPPER TROPOSPHERIC HUMIDITY

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Keywords: AEROSOL-CLOUD INTERACTIONS, DEEP CONVECTION, UPPER TROPOSPHERIC HUMIDITY, AEROSOL OPTICAL DEPTH.

INTRODUCTION

Aerosol-cloud interactions are the largest source of uncertainty in the current radiative forcing estimates of the global climate (Boucher et al., 2013). Especially processes related to deep convective clouds are yet poorly understood (Tao et al., 2012). A recent study by Riuttanen et al. (2016) shows strong observational evidence that aerosols are increasing upper tropospheric humidity (UTH). As the radiative transfer is highly sensitive to UTH (Held and Soden, 2000), this means aerosols may have a more positive radiative forcing on climate than currently taken into account in the estimates of the anthropogenic climate change.

According to models, an increase in the number of atmospheric aerosols acting as cloud condensation nuclei (CCN) leads to more numerous and smaller cloud droplets, suppressed amount of warm rain, and enhancement of ice precipitation in deep convection (Khain et al., 2005; Morrison and Grabowski, 2011; Storer and Van den Heever, 2013; Fan et al., 2013).

Ramanathan et al. (2001) suggested that aerosol-induced suppression of precipitation in the updrafts of deep clouds can transport more water into the upper troposphere. But even without changes in the total amount of precipitation, changes in cloud microphysics, namely sublimation of the increased amount of hydrometeors in the upper troposphere, can increase the UTH (Bister and Kulmala, 2011). Consistent with the proposed mechanism, more extensive and longer-lasting ice anvil clouds have been observed with larger amounts of aerosols, a sign of the increased amount of hydrometeors (Koren et al., 2005, 2010; Fan et al., 2013). High UTH has been observed to collocate with high aerosol optical depth also by Kottayil and Satheesan (2015).

METHODS

In this study we used satellite data from June, July and August in years 2007-2013. The China outflow region was chosen for a more detailed study (25-45 °N, 120-149 °E).
UTH, i.e. the relative humidity with respect to water, in a layer between approximately 200 and 500 hPa, was obtained from the microwave humidity sounder (MHS, Bonsignori (2007)) onboard the MetOp-A satellite. A microwave method developed by Buehler et al. (2008) enabled us to detect relative humidities also in the areas of anvil clouds. We used AOD from the Moderate Resolution Imaging Spectroradiometer (MODIS) instrument onboard the Terra satellite (Remer et al., 2005) and the daily rainfall product, 3B42, from the Tropical Rainfall Measuring Mission (TRMM) multisatellite analysis (Huffman et al., 2007) in this study.

The UTH data were binned according to daily precipitation in the same 1°x1° grid. The applied data were restricted to those cases when the daily precipitation was more than 1 mm. For each grid point, $\Delta UTH$ was calculated as $\Delta UTH = \text{median}[UTH(AOD\geq0.18)] - \text{median}[UTH(AOD<0.18)]$ for each precipitation bin, and an average was then calculated. 0.18 is the median of all AOD data in the study region for precipitation values of more than 1 mm day$^{-1}$.

ERA-Interim reanalysis data (Dee et al., 2011) were used to study the possible meteorological covariation of AOD and UTH in the study area. The sensitivity of the radiative transfer to perturbations in the UTH was tested by using the libRadtran radiative transfer code (Mayer and Kylling, 2005).

RESULTS AND CONCLUSIONS

Higher values of UTH were observed in association with high AOD (Table 1). Results for data with precipitation more than 1 mm day$^{-1}$ as well as with precipitation binning applied with 10 precipitation bins are shown in Table 1.

AOD was observed to increase almost linearly as a function of cirrus fraction. Linear regression was applied to AOD data in order to remove any possible data contamination by cirrus (cirrus corrected results in Table 1, rightmost column).

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<thead>
<tr>
<th></th>
<th>No cirrus correction</th>
<th>Cirrus corrected</th>
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<tbody>
<tr>
<td>$\Delta UTH$</td>
<td>5.6 ± 0.9</td>
<td>1.9 ± 0.8</td>
</tr>
<tr>
<td>$\Delta UTH$, for precipitation &gt; 1 mm day$^{-1}$</td>
<td>7.3 ±1.7</td>
<td>3.6 ± 1.8</td>
</tr>
<tr>
<td>$\Delta UTH$, for precipitation &gt; 1 mm day$^{-1}$, precipitation binning applied</td>
<td>5.8 ± 1.4</td>
<td>2.2 ± 1.5</td>
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Table 1: $\Delta UTH = UTH[AOD \geq \text{median}(AOD)] - UTH[AOD < \text{median}(AOD)]$ and is calculated for a study area east of China in June, July and August in 2007 - 2013 and is expressed as %-units. 90% confidence interval is calculated from the standard error of the monthly mean $\Delta UTH$. Cirrus correction means that cirrus fraction dependence has been removed from the AOD data.

Considerable efforts were made to study the effect of meteorological covariation or other possible causes behind the observations. We conclude that any other causes but aerosols behind the increase in UTH are very unlikely.

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REFERENCES


SESSION 4:
AEROSOL FORMATION AND GROWTH

Theo Kurtén: Accounting for chemical complexity in the formation of highly oxidized compounds by atmospheric autoxidation

Pontus Roldin: Formation and contribution of highly oxidized organic molecules to the growth of new particles

Jenni Kontkanen: Proxy for estimating the concentrations of highly oxidized organic compounds in boreal forest

Heikki Junninen: Night time observations of biogenic new particle formation over boreal fen

Katrianne Lehtipalo: The CLOUD experiment resolving the mechanism of new particle formation in boreal forest conditions

Robert Wagner: The role of ions in new particle formation in the CLOUD chamber

Xuemeng Chen: The connection and divergence of the theoretical framework for air ion study derived from the balance equation concept in the disciplines of atmospheric electricity and atmospheric aerosol study

Anna Wonashuetz: Measurement of mineral dust and organic aerosols with the LAAPTOF single particle mass spectrometer
ACCOUNTING FOR CHEMICAL COMPLEXITY IN THE FORMATION OF HIGHLY OXIDIZED COMPOUNDS BY ATMOSPHERIC AUTOXIDATION

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Keywords: secondary organic aerosol, autoxidation, volatility, saturation vapor pressure

Peroxyradical - based autoxidation mechanisms have recently been established as a potentially important source of highly oxidised, and thus potentially extremely condensable, monoterpane degradation products (Ehn et al., 2014). Due to their high polarity and molecular weight, such compounds are precisely the type of vapors needed to explain the secondary organic aerosol (SOA) formation missing from current atmospheric chemistry models (RiiPinen et al., 2011).

Most work on atmospheric monoterpane oxidation (including autoxidation) in the context of SOA formation has focused on α-pinene, as its emissions accounts for about 35% of total global monoterpane emissions (Griffin et al., 1999). Other monoterpenes such as β-pinene, limonene, and Δ3-carene have also been studied, though to a lesser extent. Similarly, OH- and O3-based oxidation have (in this context) been studied more often than NO3-based oxidation. From a chemical perspective, it is hardly surprising that different monoterpane-oxidant combinations display different behavior with respect to for example the yield of autoxidation products (and/or SOA), as well as the elemental compositions of the products. Some of these differences are easily understood based on already established reaction mechanisms: for example, OH-oxidation generally (Jokinen et al., 2015) has smaller yields of autoxidation products than ozonolysis, probably due to the (on average) greater number of oxygen atoms in the peroxyradicals formed in the latter. On the other hand, OH-oxidation typically leads to a larger variety of structures, as OH can react with monoterpenes both via hydrogen abstraction and addition mechanisms, while O3 and NO3 react solely by addition. In comparing different alkenes reacting with the same oxidant, exocyclic alkenes such as β-pinene have generally lower autoxidation product yields than analogous endocyclic alkenes such as α-pinene, likely due to fragmentation in the initial oxidant attack. In contrast, compounds with multiple double bonds such as limonene are, as expected, more reactive, and tend to have higher yields (Jokinen et al., 2015).

Some of the observed differences between monoterpenes are more difficult to explain. For example, the NO3-initiated oxidation of α-pinene in the absence of seed aerosol leads to essentially no SOA formation. In contrast, the SOA yield from NO3-initiated oxidation of Δ3-carene – which has an almost identical structure, as shown in Figure 1 – can be up to 72% (Fry et al., 2014). Our preliminary modeling work, using a recently developed cost-effective approach for addressing conformational complexity (Moller et al., 2016) suggests that the difference is related to relative branching ratios of alkoxyradical ring-breaking reactions. O3-initiated autoxidation of Δ3-carene is also likely to be more effective than that of α-pinene, as the C3 ring in the former hinders the peroxyradical hydrogen shifts to a lesser degree than the C6 ring in the latter (Kurtén et al., 2015). Neglecting chemical complexity thus proves to be dangerous: extrapolating results from α-pinene to all monoterpenes, not to mention sesquiterpenes, very likely leads to serious errors in e.g. predictions of global SOA yield.
The products of peroxyradical autooxidation likely contain multiple peroxy acid or hydroperoxide groups, and represent a new and hitherto unknown class of chemical compounds in the atmosphere. Estimates of their thermodynamic properties such as vapor pressures and solubilities are urgently needed to determine their ultimate fate, and impact on SOA formation. Unfortunately, the basis datasets of existing empirical group contribution methods for determining saturation vapor pressures do not contain complex polyhydroperoxides, and their predictions for these compounds are therefore unreliable. Our recent results (Kurtén et al., 2016) indicate that due to the strong intramolecular H-bonding of the hydroperoxide groups, autooxidation products originating from ozonolysis are much more volatile than previously assumed, and most of them are likely to be “LVOC” (low volatility organic compounds) or even “SVOC” (semi-volatile organic compounds) rather than “ELVOC” (extremely low volatility organic compounds). While LVOCs and SVOCs will still play a role in SOA formation, they will preferentially condense onto existing particles rather than form new clusters. Preliminary calculations (Berndt et al., 2016) indicate that products of OH−-initiated autooxidation may be less volatile, and could thus play a larger role for SOA, and especially new-particle formation, despite smaller overall yields compared to O3-initiated autooxidation.

REFERENCES


FORMATION AND CONTRIBUTION OF HIGHLY OXIDIZED ORGANIC MOLECULES TO THE GROWTH OF NEW PARTICLES

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Keywords: ELVOC, autoxidation, secondary organic aerosol, oligomerization

INTRODUCTION

Recent field and laboratory experiments have identified large and rapid formation of highly oxidized organic molecules (HOM) (Ehn \textit{et al.}, 2014), of which a fraction maybe extremely low-volatility organic compounds (ELVOC) (Kurtén \textit{et al.}, 2016).

METHODS

We have further developed the HOM monoterpene autoxidation mechanism proposed by Ehn \textit{et al.} (2014) and coupled it to the Master Chemical Mechanism version 3.3 (MCMv3.3, Jenkin \textit{et al.}, 1997; Saunders \textit{et al.}, 2003). The HOM formation mechanism comprises 770 reactions and 95 species. The complete gas-phase chemistry mechanism (3550 species and 10605 reactions) was implemented into the Aerosol Dynamics, gas- and particle-phase chemistry kinetic multilayer model for laboratory CHAMber studies (ADCHAM) (Roldin \textit{et al.}, 2014) and the process-based chemistry transport models ADCHEM (Roldin \textit{et al.}, 2011). We used different datasets to evaluate: (i) the HOM gas-phase formation mechanism, (ii) the potential role of HOM in new particle formation (Roldin \textit{et al.}, 2015), (iii) their contribution to the activation and growth of new particles in the atmosphere (Öström, \textit{et al.}, 2016) and (iv) how heterogeneous oligomer formation involving HOM may facilitate SOA formation.

The ADCHAM model was used to estimate the SOA formation during an $\alpha$-pinene ozonolysis, Ammonium Sulfate (AS) seed particle experiments in JPAC. ADCHAM considered condensation of all HOM species and other organic molecules from MCMv3.3 with pure liquid saturation vapour pressures ($p_0$) $< 10^{-2}$ Pa. The HOM $p_0$ were either estimated with the functional group contribution method SIMPOL (Pankow and Asher, 2008) or based on detailed quantum-chemistry continuum solvent model COSMO-RS (CONductor-like Screening MOdel for Real Solvents) calculations (Kurtén \textit{et al.}, 2016). $p_0$ estimated with COSMO-RS are generally substantially higher than what is predicted by SIMPOL. Because the pure liquid saturation vapor pressures from COSMO-RS has not been calculated for all HOM species considered by the HOM mechanism we derived correction factors based on the difference between the SIMPOL and COSMO-RS $p_0$ reported Kurtén \textit{et al.} (2016). For the HOM monomers the correction factor is $10^{2.8\text{O:C}-0.1}$, where O:C is the oxygen-to-carbon ratio. For the HOM dimers we estimated a fixed correction factor of $10^{3}$ (see Öström \textit{et al.}, 2016 for details).

ADCHEM was operated as a 1D (vertical column) trajectory model along air mass trajectories reaching the measurement stations Pallas (67.97° N, 24.12° E) and Hyytiälä (61.85° N, 24.28° E). The model results were evaluated using measured particle properties and HOM gas-phase concentrations.
RESULTS AND CONCLUSIONS

Figure 1 shows the modelled and measured (a) HOM(g) concentration and (b) HOM dimer mole fraction during an experiment with varying α-pinene + O\textsubscript{3} reaction rates in the Jülich Plant Atmosphere Chamber (JPAC). The HOM were measured with high-resolution chemical ionization mass spectrometer (CI-APi-TOF), see Ehn et al., (2014) for details. At α-pinene + O\textsubscript{3} reaction rates >0.5 p.p.t s\textsuperscript{-1} the model captures the observed slowly increasing HOM dimer gas-phase concentrations with increasing reaction rates (Figure 1b). However, at lower α-pinene + O\textsubscript{3} reaction rates the model seem to underestimate the HOM dimer fraction during the experiment. In the model HOM(g) dimers are formed by peroxy radical (RO\textsubscript{2}) termination via RO\textsubscript{2} + RO\textsubscript{2} reactions. However, at low RO\textsubscript{2} concentrations in the chamber most RO\textsubscript{2} are instead reacting with HO\textsubscript{2} or NO and form HOM monomers.

Figure 1. Modelled and measured (a) HOM(g) concentration and (b) HOM(g) dimer mole fraction as a function of the α-pinene + O\textsubscript{3} reaction rate in the JPAC chamber.

Figure 2 shows results from an α-pinene ozonolysis, Ammonium Sulfate (AS) seed particle experiments in JPAC. In figure 2a we compare the modelled and measured HOM(g) monomer mole fraction evolution during the seed particle addition. The observed substantial increase in the HOM(g) monomer mole fraction when the seed particle are introduced indicates that not all HOM monomers are true ELVOCs. Figure 2b shows the modelled and measured SOA formation during the seed particle addition and how the HOM(g) concentration is decreasing when the seed particles are added to the chamber.

When the HOM \(p_0\) are estimated with SIMPOL the model slightly underestimates the SOA formation during the experiment (Figure 2b) and substantially underestimates the HOM(g) monomer mole fraction change caused by the seed particle addition (Figure 2a). With \(p_0\) estimated based on the COSMO-RS calculations the SOA formation is underestimated substantially (Figure 2b) and the model now overestimates the HOM(g) monomer mole fraction change during the seed particle addition (Figure 2a). However, if we also assume that all condensable organic molecules are involved in relatively rapid heterogeneous oligomerization reactions, we can get both the modeled SOA formation, HOM(g) concentration evolution and HOM monomer mole fraction evolution to agree very well with the observations when using the \(p_0\) based on the COSMO-RS. For the results presented in figure 2 we used a heterogeneous dimer formation rate of \(3 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}\).
Figure 2. Modeled and measured (a) HOM(g) monomer mole fraction and (b) SOA formation and HOM(g) concentration during a Ammonium Sulfate (AS) seed particle experiments in the JPAC chamber (Ehn et al., 2014).

Figure 3. Modelled and measured average diurnal trends of (a) HOM(g) monomers, (b) HOM(g) dimers, (c) HOM(g) RO2 and (d) total HOM(g) concentrations at Hyytiälä 15th to 24th of May, 2013.
Figure 3 shows the modelled and measured average diurnal pattern of (a) the HOM(g) monomers, (b) HOM(g) dimers, (c) HOM(g) RO$_2$ and (d) total HOM(g) concentration from Hyytiälä, 15$^{th}$ of May to 24$^{th}$ of May, 2013. Based on the ADCHAM model results presented in figure 2, ADCHEM was operated using HOM$_{p_0}$ estimated based on COSMO-RS and a heterogeneous dimer formation rate of $3 \times 10^{-3}$ M$^{-1}$ s$^{-1}$. The HOM measurements were performed with a similar CI-API-TOF instrument setup as was used in the JPAC chamber by Ehn et al. (2014). The model and measured HOM(g) concentrations are highly correlated, with correlation coefficients of 0.71 for the HOM monomers, 0.80 for the HOM dimers, 0.67 for the HOM RO$_2$ and 0.74 for the total HOM(g) concentration. The modeled average total HOM(g) gas-phase concentration is 0.81 p.p.t. and the measured 0.63 p.p.t. The model mainly overestimates the HOM(g) concentration during the night when the modeled HOM(g) concentration is sensitive to the boundary layer mixing height and the slow vertical mixing rate.

With the newly developed and constrained HOM formation mechanism ADCHEM captures the main features of the observed particle number size distribution evolution during new particle formation events at the Pallas field station in northern Finland when the HOM$_{p_0}$ were estimated using SIMPOL, but underestimates the particle growth when using $p_0$ based on COSMO-RS (Öström et al., 2016). In this study we did not consider the contribution of heterogeneous oligomerization for the particle growth. According to the model results from Pallas, about 70 % of the nucleation model particle volume is SOA formed from HOM, 20 % from other VOC included in MCMv3.3 and 10 % from ammonium sulphate. We are currently performing similar ADCHEM model simulations for Hyytiälä during the spring 2014 where we will evaluate how sensitive the modelled activation and growth of new particles are to the HOM$_{p_0}$ and heterogeneous oligomerization. We will also test if heterogeneous oligomerization can further improve the agreement between the modelled and measured particle number size distributions during the simulated new particle formation events at Pallas.

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REFERENCES

PROXY FOR ESTIMATING THE CONCENTRATIONS OF HIGHLY OXIDIZED ORGANIC COMPOUNDS IN BOREAL FOREST

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Keywords: highly oxidized organic compounds, monoterpenes, boreal forest

INTRODUCTION

Terrestrial ecosystems emit large amounts of volatile organic compounds into the atmosphere (Günther et al., 2012). In boreal forests, these emissions are dominated by monoterpenes, which form highly oxidized multifunctional organic compounds (HOMs) when they are oxidized in the atmosphere (Ehn et al., 2012; Jokinen et al., 2014). Recent laboratory studies indicate that these compounds can participate in new particle formation and growth, and thus affect global CCN (cloud condensation nuclei) concentrations (Ehn et al., 2014; Jokinen et al., 2015; Kirkby et al., 2016; Tröstl et al., 2016). HOMs can be detected using high-resolution chemical ionization mass spectrometry techniques (Jokinen et al., 2012). However, so far only short-term measurements of atmospheric HOM concentrations are available.

In this study our aim is to develop proxies, which can be used for estimating HOM concentrations in the boreal forest environment. We utilize a proxy of the total concentration of monoterpenes oxidation products presented by Kontkanen et al. (2016), which includes the oxidation of monoterpenes by O3, OH, and NO3. We compare this proxy to the HOM concentrations measured with a nitrate-based chemical ionization atmospheric-pressure-interface time-of-flight mass spectrometer (CI-API-TOF) and determine the yields for each reaction which produce the best agreement between the proxy and measurements.

METHODS

The CI-API-TOF measurements were conducted between 8 April and 28 June 2013 at the SMEAR II station in Hyytiälä, Finland. From these measurements, the concentrations of HOMs were calculated for two mass-to-charge ranges: 260–450 Da (here referred to as HOM monomers, mostly C10 compounds) and 451–622 Da (here referred to as HOM dimers, mostly C20 compounds).

By assuming that the limiting step of the HOM formation is the first oxidation step of monoterpenes, the proxy for HOM concentrations can be written as (Kontkanen et al., 2016):

\[
HOM_{proxy} = \frac{(y_{O3}k_{O3+MT}[O_3]+y_{OH}k_{OH+M}[OH]+y_{NO3}k_{NO3+MT}[NO_3]) \times MT_{proxy}}{CS}
\]  

(1)

Here \(k_{O3+MT}, k_{OH+MT}, \) and \(k_{NO3+MT}\) are the temperature-dependent reaction rate coefficients between monoterpenes and different oxidants. \([O_3]\) is the measured ozone concentration, \([OH]\) is the concentration of hydroxyl radical estimated based on UV-B radiation (Petäjä et al., 2009), and \([NO_3]\) is the concentration of nitrate radical estimated according to Peräkylä et al. (2014). \(MT_{proxy}\) is the monoterpenone concentration estimated from a proxy by Kontkanen et al. (2016; Eq. 12). CS is the condensation sink, which is calculated from particle size distribution data (Kulmala et al., 2001). \(y_{O3}, y_{OH}, \) and \(y_{NO3}\) describe the molar yields of oxidation products from each reaction. In Kontkanen et al. (2016), these yields were assumed to equal 1. In this work, the values for the yields were obtained by minimizing the variability of the ratios between the proxy and measured HOM concentrations. The variability was determined as the ratio between 90th and 10th percentiles \(V_{90/10}\) of the proxy-to-measurements ratios (Paasonen et al., 2010; Kontkanen et al., 2016). The optimization was performed separately for HOM monomers and HOM dimers.
RESULTS

Figure 1 shows the correlations between the optimized proxies and measured HOM concentrations for HOM monomers and dimers. The proxies seem to correlate rather well with measured concentrations in both mass ranges. The correlation coefficient obtained between the proxy and measurements is higher for HOM dimers ($R = 0.64$) than for monomers ($R = 0.43$). Similarly, the variability of the proxy-to-measurement ratios is lower for HOM dimers ($V_{90/10} = 5.1$) than for monomers ($V = 8.4$).

The molar yields obtained for HOM monomers and dimers for each reaction are presented in Table 1. For HOM monomers, the yield obtained for the OH reaction is about two times higher than the yields for O$_3$ and NO$_3$ reactions. On the other hand, for HOM dimers the highest yield is obtained for O$_3$ and NO$_3$ reactions, and the yield for the OH reaction is clearly lowest. This indicates that different oxidation pathways are important in the formation of HOM monomers and dimers in boreal forests.

CONCLUSIONS AND OUTLOOK

We developed proxies for estimating HOM concentrations at a boreal forest site by utilizing CI-API-TOF measurements. Our proxies correlate reasonably with the measured HOM concentrations. In the future we will include longer data set of CI-API-TOF measurements in the analysis and investigate the performance of the proxies to predict HOM concentrations in different mass ranges in more detail.

Table 1. The molar yields obtained for different reactions by minimizing the variability of the proxy-to-measurement ratios for HOM monomers and dimers.

<table>
<thead>
<tr>
<th></th>
<th>$Y_{O3}$</th>
<th>$Y_{OH}$</th>
<th>$Y_{NO3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HOM_{proxy, monomers}$</td>
<td>0.13</td>
<td>0.30</td>
<td>0.14</td>
</tr>
<tr>
<td>$HOM_{proxy, dimers}$</td>
<td>0.018</td>
<td>0.001</td>
<td>0.011</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

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REFERENCES

Ehn, M et al. (2012). Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air, Atmos. Chem. Phys., 12, 5113-5127.
Petäjä, T. et al. (2009). Sulfuric acid and OH concentrations in a boreal forest site, Atmospheric Chemistry and Physics, 9, 19, 7435-7448.
Peräkylä, O. et al. (2014). Monoterpenes’ oxidation capacity and rate over a boreal forest: temporal variation and connection to growth of newly formed particles, Boreal Environment Research, 19, 293-310
NIGHT TIME OBSERVATIONS OF BIOGENIC NEW PARTICLE FORMATION OVER BOREAL FEN

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Keywords: VOC, ELVOC, CI-API TOF, atmospheric new particle formation, wetland.

INTRODUCTION

Formation of new aerosol particles in the atmosphere is a complicated series of chain reactions, including the production of nanometre-size clusters from precursor vapours, the growth of these clusters to detectable sizes by condensation and the simultaneous removal of clusters by coagulation. New particle formation has been observed throughout the globe (Kulmala, et al. 2004). It is thought that sulphuric acid is critical in initialization of the particle formation (Kuang, et al. 2008, Kulmala, et al. 2013), except in certain coastal regions where iodine oxides are dominating the process (Sipila, et al. 2016). Recent laboratory studies hypothesise that pure organic ion-induced new particle formation could potentially happen also in atmospherically relevant conditions (Kirkby, et al. 2016) and signs of this has been observed in boreal forest (Lehtipalo, et al. 2011) and in the High Alps (Bianchi, et al. 2016).

It is known that wetlands are warming the climate due to the methane emission even though, they act also as a carbon sinks by up-taking the CO₂ (Rinne, et al. 2007). The amount and composition of Biogenic Volatile Organic Compounds (BVOCs) emitted from arctic wetlands in changing climate is to be of high importance since about half of global wetlands are located between 50 and 70°N and they constitute approximately half the arctic vegetated area (Walker, et al. 2005). Related, the capability of emitted BVOC to participate in particle formation is greatly dependent on the composition of BVOCs. It has been shown that temperature treatment of arctic wetland changes the composition of BVOC emissions (Lindwall, et al. 2016).

In this study, we measured the composition of BVOC emissions from a wetland, depletion of O₃ and formation of the oxidation products of emitted BVOCs. We also show the involvement of produced low volatile organic compounds in atmospheric new particle formation.

METHODS

The measurement campaign was conducted in boreal wetland close to SMEAR II station, the time period of the campaign was from 11th of March to 20th June 2016. The measurement site is situated on a sedge fen in southern Finland (61.8327N, 24.1928E, 162 m a.s.l.). Peat depth ranges from 2m near the upland forest edge to almost 4m at the center of the site. The vegetation of the site, being dominated by different sedges and a continuous Sphagnum carpet. The site is surrounded by Scots pine forest (Aurela, et al. 2007). The fen acts as a source of methane throughout the year with the maximum during the summer time and minimum during the coldest season (annual emission +12.6 g m⁻², equals +9.4g·C m⁻²). The methane emissions have a temporal pulse in spring time during the snow melt period and are not showing any diurnal variation during any season. The CO₂ fluxes in contrary have a negative annual balance -156 g m⁻², equals -42.5 g·C m⁻² (Rinne, et al. 2007).
The site is equipped with permanent measurements for basic meteorology and specially, for CO₂, H₂O, and CH₄ fluxes. For the campaign a special cabin on a pier was built and was equipped with advanced instrumentations. Chemical composition of atmospheric ions was measured with atmospheric pressure interface time-of-flight mass spectrometer (API-TOF, (Junninen, et al. 2010)), concentrations of sulfuric acid (SA) and low volatile oxygenated organics (highly oxidized multifunctional molecules, HOM) with chemical ionization with nitrate chemistry (NO3-Cl-API-TOF (Jokinen, et al. 2012). Volatile organic compounds (VOC) were measured with proton transfer reaction (PTR)-TOF. Atmospheric cluster and aerosol size distribution was measured with Neutral clusters and Air Ion Spectrometer (NAIS) (Mirmé, et al. 2007) and nano-particles <2nm with particle size magnifier (PSM) (Vanhana, et al. 2011).

CONCLUSIONS

During the campaign, we observed several new particle formation events. The ones observed during the day time had the same characteristics as the ones observed in SMEAR II measurement station (Hari and Kulmala 2005) 10km away. In these day time particle formation events the sulphuric acid is the one single most increasing component (Kulmala, et al. 2013). However, during the night time events the observed chemistry was considerably different. The most prominent difference was decrease of O₃ concentration from 30-50 ppb to as low as 2-5 ppb. At the same time the concentration of SA was decreasing, as expected, with the decreasing solar radiation, but concentrations of smaller HOMs (m/z < 450Th) and specially the larger HOMs (m/z >450Th) increased by order of magnitude. Also, the concentration of small ions increased at the same time and in some cases even the growth up to 40nm (upper limit of measurements) was observed. Same time the nitrate containing HOMs decreased. This behaviour points towards a purely organic oxidation and formation of new particulates, without involvement of SA or NOₓ.

These events became more frequent after the snow melt and the increased temperature difference between day and night. Low relative humidity and low wind speeds are also associated with the observed night time organic new particle formation events.

In the presentation observed organic oxidation and consecutive new particle formation will be discussed in details.

ACKNOWLEDGEMENTS

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REFERENCES

Hari P. and M. Kulmala (2005) "Station for measuring ecosystem-atmosphere relations (SMEAR II)." Boreal Environment Research 10 (5) 315-322


THE CLOUD EXPERIMENT RESOLVING THE MECHANISM OF NEW PARTICLE FORMATION IN BOREAL FOREST CONDITIONS

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Keywords: NEW PARTICLE FORMATION, NUCLEATION, CHAMBER EXPERIMENTS.

INTRODUCTION

Even though new particle formation (NPF) is known to be a major source of atmospheric aerosols and cloud condensation nuclei, the exact physical and chemical mechanisms behind it are poorly understood. Due to a large amount of co-varying factors in the atmosphere, laboratory experiments are crucial in isolating the effect of different chemical compounds and environmental parameters on NPF.

Previous CLOUD (Cosmics Leaving OUtdoors Droplets) experiments have concentrated on binary nucleation from sulphuric acid and water (Kirkby et al. 2011; Duplissy et al. 2016), ternary nucleation of sulphuric acid and water together with ammonia (Kirkby et al. 2011; Dunne et al. 2016) or dimethylamine (Almeida et al. 2013) and pure biogenic nucleation from alpha-pinene (Kirkby et al. 2016). These studies, however, did not cover the interactions between these systems, which could be important especially in the atmospheric boundary layer. Although both pure biogenic nucleation and ternary nucleation are plausible mechanisms of new particle formation in the atmosphere, neither of them alone can explain all of the observed NPF events in the boreal forest.

The main aim of this study is simulating the new particle formation process observed at the Hyytiälä SMEAR II station, which is one of the most studied field sites in respect of NPF. This was done by conducting experiments in the CLOUD chamber in the simultaneous presence of multiple precursor vapors and oxidation pathways, while at the same time, maintaining a high degree of control and a low level of contaminants, which are characteristic for the CLOUD experiment.

METHODS

The experiments described here took place at the CERN CLOUD chamber facility during the 12-week CLOUD10 campaign in fall 2015. Additional experiments were conducted during the CLOUD11 campaign in fall in 2016.

As precursors for particle formation we used the two most abundant monoterpenes in the boreal forest: alpha-pinene and delta-3-carene, individually or as their mixture. The total monoterpene volume mixing ratio was varied from about 150 to 1200 ppt. The experiments were conducted at varying levels of SO$_2$ (leading to sulfuric acid concentrations from less than 1e5 cm$^{-3}$ up to about 1e8 cm$^{-3}$) and NO$_x$ (from 0 to 5...
ppb). The ozone concentration was kept constant (at ca. 40 ppb), while the OH concentration was varied by changing the UV light intensity. The first set of experiments was carried out without ammonia to ensure clean conditions in the chamber, and later 200-400 ppt of ammonia was added. All of the experiments were done first in neutral conditions (removing all ions artificially from the chamber by applying an electric field) and then repeated with ionization from natural galactic cosmic rays (GCR) and sometimes with additional ionization from the CERN pion-beam to study the fraction of ion-induced nucleation. Figure 1 presents a conceptual picture of the experiment and table 1 lists the combinations of precursor vapors studied.

A comprehensive suite of instruments, including state-of-the-art particle counters and mass spectrometers, was used to detect the forming particles and their precursors. The particle number concentration and size distribution were measured with several PSMs and CPCs, the DMA-train, the NAIS and several SMPS-systems. The particle formation rate and size dependent growth rates were retrieved from these measurements. The concentration of precursor vapors and oxidants were measured with gas monitors, several high-resolution chemical ionization mass spectrometers and the PTR-TOF. The APi-TOF was used to determine the composition of negative and positive ion clusters.

Figure 1. Conceptual picture of the CLOUD experiments simulating particle formation in Hyytiälä. The most important trace gases added to the chamber are indicated on the left side of the chamber, while the main environmental variables controlled during the experiments are indicated on the top.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>System I</th>
<th>System II</th>
<th>System III</th>
<th>System IV</th>
<th>System V</th>
<th>System VI</th>
<th>System VII</th>
</tr>
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<tbody>
<tr>
<td>Alpha-pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Delta-3-carene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
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<td>SO2</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOx</td>
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<td>x</td>
<td></td>
<td></td>
<td>x</td>
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</tr>
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<td>NH3</td>
<td></td>
<td></td>
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<td></td>
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<td>x</td>
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</tr>
<tr>
<td>T (ºC)</td>
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<td>5</td>
<td>5</td>
<td>-25, 5, 25</td>
<td>5</td>
<td>5</td>
<td>5, 25</td>
</tr>
</tbody>
</table>

Table 1. A list of different chemical systems explored during CLOUD10 (Hyytiälä runs)
CONCLUSIONS

We will present the first results from the “Hyytiälä simulation” in the CLOUD chamber and show how new particle formation can proceed simultaneously by pure biogenic pathway and by acid-base mechanism. We will show that sulfuric acid, ammonia, nitrogen oxides and organics are all needed for replicating the nucleation and growth rates and their variability observed in the boreal forest environment. Mass spectrometry data is used to confirm the proposed nucleation mechanisms. We will also discuss the observed effect of NO_x (see also Yan et al., this abstract collection) and ions (see also Wagner et al., this abstract collection) on the NPF process in the different chemical systems.

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REFERENCES


THE ROLE OF IONS IN NEW PARTICLE FORMATION IN THE CLOUD CHAMBER

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Keywords: NEW PARTICLE FORMATION, IONS, CHAMBER STUDIES, CLOUD.

INTRODUCTION

The CLOUD chamber facility (Kirkby et al. 2011; Dullissy et al. 2016) located at CERN enables the study of the effect of different levels of ionizing radiation on new particle formation. It is equipped with a high voltage field cage (clearing field) that can be used to remove all ions from the chamber. One of the key features of the CLOUD experiment is the extremely low level of contaminants, which allows the investigation of new particle formation in different chemical regimes under precisely defined conditions. While ion concentrations have been found to affect nucleation rates in previous studies (Kirkby et al. 2011; Almeida et al. 2013; Riccobono et al., 2014; Dullissy et al., 2016; Kirkby et al. 2016; Dunne et al., 2016; Kuerten et al., 2016) the size-resolved charge fractions were not yet subject to a detailed study. With a broad set of experiments covering abundant chemical compounds like monoterpenes, sulfuric acid, nitrogen oxides and ammonia, we aim to shed light on the significance of ion mediated nucleation processes in different environments.

METHODS

In one of the most recent measurement campaigns (CLOUD10, Sep-Dec 2015) we used a novel instrument setup to study the effect of charges on the formation of clusters. We operated two particle size magnifiers (PSM, Airmodus Ltd., model A11) in parallel, removing the ions from the sample for one of the PSMs (Kangaslouma et al. 2016). This way we were able to directly measure the charging state of the formed clusters. A sample experiment for the assessment of nucleation rates in the presence of ions is displayed in Fig. 1. Before the experiment, ions are removed from the chamber; only a small background concentration is detected and the concentration of total and neutral particles is the same (within error limits). When the clearing field was switched off and alpha pinene was injected into the chamber at 23:57, the concentration of ions increased and a strong signal of ion-induced particle formation was observed.

In addition to particle counters and an ion spectrometer (NAIS), a set of mass spectrometers and sensitive gas monitors measured the chemical composition of newly formed clusters and their precursors. Regimes studied include a mixture of monoterpenes (α-pinene, Δ-3-carene; 100–1500 pptv), sulfuric acid (<10^2–7×10^8 cm^-3), nitrogen oxides (0–5 ppbv) as well as ammonia (0–3 ppbv).
RESULTS

We observed that particles are likely to be charged when they are very small (1.2 nm in diameter) and when conditions for nucleation are not favorable (e.g., low precursor gas concentrations). In these situations, a charge can stabilize the cluster, and ions are important for new particles to form.

As the particles grow to slightly larger sizes (1.7 nm), many of the initially charged clusters become more stable and get neutralized by recombination. When they reach a diameter of 2.2 nm, almost all of the particles are neutral. However, we found the influence of recombination to be strongly dependent on the concentration of cluster ions, which was higher in our study than in comparable conditions at ground level in the atmosphere (coagulation sink).

In our experiments we studied five chemical environments, from pure biogenic vapors to conditions similar to Hyytiälä, Finland, investigating the effects of monoterpenes, sulfuric acid, nitrogen oxides, and ammonia.

![Number size distribution, negative ions](image1)

![Cluster ion concentration](image2)

Figure 1. Ion-induced particle formation at 25°C from 900 pptv alpha pinene. The time evolution of a) number size distribution of negative ions, and b) cluster ion concentration (0.8 - 1.7 nm) in the NAIS are displayed. The clearing field is switched off at 23:57 (dashed line).

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REFERENCES

THE CONNECTION AND DIVERGENCE OF THE THEORETICAL FRAMEWORK FOR AIR ION STUDY DERIVED FROM THE BALANCE EQUATION CONCEPT IN THE DISCIPLINES OF ATMOSPHERIC ELECTRICITY AND ATMOSPHERIC AEROSOL STUDY

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Keywords: ionising radiation, air ions, ion balance, ion formation rate.

INTRODUCTION

Air ions are airborne substances that carry electric charge in the atmosphere (e.g. Hirskikko et al., 2011). Owing to the presence of the ionosphere, there exists a naturally-occurring electric field in the Earth-atmosphere system (e.g. Tinsley, 2008). Motions of air ions in this electric field result in the electrical conductivity of air (Harrison, 2001). The study of the air conductivity lays the foundation of the atmospheric electricity discipline, where the original attention paid to air ions manifests itself (Israël, 1970). During the development of the understanding on atmospheric electricity, there emerged observations on the relation of air ions to the formation of cloud droplets (Wilson, 1895, 1899). These findings evoked the interest in air ions from the atmospheric aerosol community.

AIR IONS IN THE ATMOSPHERIC ELECTRICITY AND ATMOSPHERIC AEROSOL APPROACHES

Ionising radiation creates initial charge carriers by ionising air molecules. Via a series of dynamic processes, including both chemical reactions and physical transformations, a fraction of these initial charge carriers can pass their electric charges to more stable air ions (e.g. Chen et al., 2016). Based upon the theoretical understanding of air ion formation from ionising radiation, mathematical models have been proposed to describe the ion balance between the ion production rate/ionisation rate ($J$) and measured air ion concentrations (Harrison, 2001; Israël, 1970; Tammet et al., 2006). These models are typically built on a quasi-steady state assumption. This is the traditional ion balance approach that stems from the atmospheric electricity study.

For the study of atmospheric aerosols, the topic of new particle formation (NPF) is of primary importance, for the NPF process supplements aerosol particles in the air (Poschl, 2005). Air ions are known to take part in NPF (Kulmala & Kerminen, 2008), which is customarily referred as ion-induced or ion-mediated NPF (Yu & Turco, 2008). The formation rate of charged particles in a certain measurable size range ($J$) is typically used to characterise NPF processes involving air ions (Kulmala et al., 2012). To its root, the $J$ determination originates from the balance equation concept, where the formation rate balances with the recombination, coagulation and condensation loss rates of the charged particles (Kulmala et al., 2004).
ION BALANCE AND SENSIBILITY STUDIES

Apparently, $J$ and $I$ share the same origin from the ion balance concept. However, the connection between $I$ and $J$ remains unclear. $I$ takes typically a value of about 10 cm$^{-3}$s$^{-1}$ (Chen et al., 2016; Harrison & Carslaw, 2003), whereas $J$ is usually found in the range of 0.01-1 cm$^{-3}$s$^{-1}$ (Nieminen et al., 2011). In this work, the balance equation is reviewed to investigate the linkage between $I$ and $J$. By a term-to-term comparison of $I$ and $J$ determination approaches, we aim to consolidate the theoretical framework for air ion study from both the atmospheric electricity and atmospheric aerosol disciplines.

With an updated ion balance theory, the validity and reliability of the rate coefficients used in the balance equation are evaluated with an emphasis on the identification of the future needs for parameterisation. Moreover, the feasibility for an ion closure auditing is assessed based on ambient measurement data collected from the SMEAR II station. The station locates in a boreal forest in southern Finland (61°51’ N, 24°17’ E; 181 m above sea level) (Hari & Kulmala, 2005). Air ion data and ionising radiation data collected during years 2003-2006 are used in ion balance assessment. The air ion data were measured by a Balanced Scanning Mobility Analyser (BSMA) and the ionising radiation data were recorded by a radon monitor and a gamma spectrometer (Chen et al., 2016).

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REFERENCES


MEASUREMENT OF MINERAL DUST AND ORGANIC AEROSOLS WITH THE LAAPTOF SINGLE PARTICLE MASS SPECTROMETER

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Keywords: single particle mass spectrometry, mineral dust, organic aerosol

INTRODUCTION

Single particle aerosol mass spectrometry is a method for the time- and size resolved measurement of aerosol chemical composition on a single-particle basis. Laser ablation instruments are able to detect refractory aerosol components such as mineral dust and elemental carbon, in addition to non-refractory components such as many organic aerosol compounds. The Laser Ablation Aerosol Particle Time-of-Flight mass spectrometer (LAAPTOF, AeroMegt, GmbH) is a new, commercially available instrument of this kind. In this study, we present measurements of different types of aerosols with the LAAPTOF during the Fifth Ice nucleation (FIN 01) workshop mass spectrometer intercomparison campaign at the Karlsruhe Institute of Technology. We report performance parameters such as detection efficiencies, size range, hit rates, as well as sample spectra of the different aerosol types.

METHODS

The LAAPTOF uses the scattering of light by two 405 nm detection lasers to detect single particles, laser ablation to ionize them, and a bipolar ToF mass spectrometer to detect the resulting positive and negative ions and fragments. The flight time of the particles between the two detections lasers is measured and, with a suitable calibration, used to determine particle size. The LAAPTOF has undergone some changes since earlier descriptions (Gemayel et al., 2016, Marsden et al., 2016), most notably the installation of a new ablation laser (ATLEX 300/500 I, ATL Lasertechnik GmbH). During FIN 01, the LAAPTOF mass spectrometer (AeroMegt, GmbH) was sampling a range of different generated aerosols from the AIDA (Aerosol Interactions and Dynamics in the Atmosphere) and APC (Aerosol Preparation and Characterization) chambers (Möhler et al, 2003, Gallavardin et al., 2008). The instrument was aligned and calibrated for particle size with standard PSL particles; mass calibration was performed with a suspension of carbon black in a water/isopropanol mixture. The single particle spectra were analyzed using a fuzzy clustering algorithm, which groups the spectra by similarity and calculates central spectra representing the groups.
CONCLUSIONS

15 different types of aerosols, including different coated and uncoated mineral dust types, bacteria, and secondary aerosol components were sampled successfully. First results show that detection and hit rates (the fraction of detected particles resulting in actual mass spectra) depend on the type and concentration of the sample. Hit rates of 77.6% were found for 599 nm PSL particles, between 45 and 50% for bacteria samples, and dropped to below 30% for some mineral dusts. For mineral dusts, many positive spectra showed saturation effects. Sulfuric acid coatings on mineral dust particles were detected (Fig 1).

REFERENCES


SESSION 5: 
AEROSOL-CCN-CLOUD

Xiangrui Kong: Adsorption, dissociation and diffusion of HCl at the warm ice surface and beyond

Jurgita Ovadnevaite: The role of organics in marine aerosol CCN activation

Luke Cravigan: Sources of cloud condensation nuclei over the remote Southern Ocean

Paul Herenz: CCN measurements at the Princess Elisabeth Antarctica Research Station

Risto Makkonen: Global trends of cloud condensation nuclei concentrations

Simon Gruber: Climate engineering by Arctic winter cirrus thinning: risks and feasibility

James Hudson: Accumulation mode from cloud processing

Shani Tiwari: Aerosol effect on warm cloud properties over Central Indo-Gangetic Basin
THE FATES OF HCl ON WARM ICE

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Keywords: warm ice, HCl, dissociation, depth profile, XPS, NEXAFS.

INTRODUCTION

Ice and snow play active roles for the water cycle, the energy budget of the Earth, and environmental chemistry in the atmosphere and cryosphere. Trace gases can be taken up by ice, and physical and chemical fates of the impurities could modify surface properties significantly and consequently influence atmospheric chemistry and the climate system. However, the understanding of chemical behaviour of impurities on ice surface remains very poor. Strong acids and ice interactions have drawn scientific attentions for many years, e.g. acidic gases playing a pivotal role in stratospheric ozone depletion and halogen chemistry. As the importance of the equilibrium lies in chemical reaction, it is crucial to track the fates of strong acids on warm ice with direct experimental evidences, which may lead to rethinks of the roles that acids play in environment. In this study we aim to answer the following key questions that are still open: 1) Can molecular HCl survive on warm ice? If so, 2) Do undissociated HCl and the dissociated Cl\textsuperscript{-} behave differently on/in ice? 3) Where does the acid dissociate? 4) Will HCl/Cl\textsuperscript{-} disorder the ice structure?

METHODS

We employed synchrotron-based X-ray photoelectron spectroscopy (XPS) and partial electron yield Near Edge X-ray Absorption Fine Structure (NEXAFS) in a state-of-the-art near-ambient pressure photoelectron (NAPP) spectroscopy end station. The NAPP enables to utilize the surface sensitive experimental methods, XPS and NEXAFS, to be used on volatile surface such as ice at -20°C, where HCl adsorption, dissociation and diffusion on and in ice were tracked.

CONCLUSIONS

It was surprising to find that HCl largely retains its molecular form on warm ice at -20°C. A three-layer model was used to quantitatively fit the depth profiles of both molecular HCl and dissociated Cl\textsuperscript{-}, where we found that an ionic Cl\textsuperscript{-} reservoir layer located underneath the topmost interface. HCl-induced hydrogen bond network distortion is also directly measured, and the disordered layer has both liquid- and solid-like features. An integrated picture of the life cycle of HCl on ice is drawn. The newly obtained evidence supports not only the understanding of the behavior of HCl or other strong acids on ice but also shed light on the chemical properties of quasi liquid layer on ice.
THE ROLE OF ORGANICS IN MARINE AEROSOL CCN ACTIVATION

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Keywords: Organic Matter, CCN, Marine Aerosol.

INTRODUCTION

Marine aerosol occurring in cloud condensation nucleus (CCN) sizes suggest that it may contribute notably to the CCN population (Meskhidze et al., 2006; Sorooshian et al., 2009), but further cloud droplet number concentration would strongly depend on the chemical aerosol composition and ambient (cloud) conditions, such as available water content, supersaturation and competition between the CCN of different composition (O'Dowd et al., 1999). Since the global importance of marine aerosol particles to the cloud formation postulated several decades ago (Charlson et al., 1987), it has progressed from the evaluation of the nss-sulphate and sea salt effects to the acknowledgement of the significant role of organic aerosol (O'Dowd et al., 2004). It was demonstrated that primary marine organics, despite its hydrophobic nature, can possess the high CCN activation efficiency, resulting in the efficient cloud formation (Ovd네vaite et al., 2011). Organic aerosol, ubiquitous in both the clean and polluted atmosphere, can be present as a pure organic aerosol or and internally-mixed aerosol with other constituents such as sulphate and nitrate aerosol (Kanakidou et al., 2005; Fuzzi et al., 2006). The hygroscopicity of organic aerosol in sub-saturated humidity fields is typically less than most common salts found in the atmospheric aerosol (Liu et al., 2010); however, the ability of organic aerosol to activate cloud droplets is predicted to be greatly increased in supersaturated air due a lowering of the droplets surface tension, ultimately leading to more nuclei being activated at lower supersaturations (Facchini et al., 2000). While this phenomenon has been acknowledged for some time, it has yet to be demonstrated in the real atmosphere.

There are two major sources of marine organics –primary sea spray production and secondary new particle formation. For the latter, organics can play a role in both formation and growth of the newly formed particles. We have previously reported that new particle production occurs over the open North Atlantic Ocean in polar marine air masses (Monahan et al., 2010). During these new particle production events, the new particle mode typically injects 1,500-2,500 cm-3 new particles into the sub-100 nm size range and over spatial scales ~1,500 km, resulting in approximate 4-fold increase in number concentration and, thus, potentially CCN. Here we study the organic effect on primary and secondary marine aerosol activation to CCN. Results from two intensive measurement campaigns in the Eastern North Atlantic (Mace Head) and the Southern Ocean (PEGASO cruise) are presented here with the main focus on CCN dependence on aerosol chemical composition and, especially, origin and sources of marine organic. We investigate the activation of sea spray composed of the sea salt and externally mixed with nss-sulphate as well as the sea spray highly enriched in organics, stressing the importance of the latter to the formation of the cloud droplets. In addition, the organic effect on CCN activation of newly formed marine particles is investigated. Moreover, the suitability of existing theories to explain the marine aerosol activation to CCN is explored.

METHODS

CCN measurements were performed with a DMT CCN counter as well as a miniature Continuous Flow Streamwise Thermal Gradient Chamber, which measure the fraction of aerosol that act as a CCN for a range of supersaturations. During this study, the supersaturation spanned from 0.1% to 1 % for the former and 0.2% to 0.82% for the latter. To perform a closure exercise, CCN concentrations were also calculated using κ-Köhler theory (Petters et al., 2007) where the critical activation diameter (Dc) and κ calculations
were constrained by AMS-derived chemical composition along with documented hygroscopic growth-factors for specific compounds (1.1, 1.8, 1.5, 2.4, 1.57 corresponded to OM, sulphate, nitrate, sea salt and MSA, respectively) and associated relationships between growth-factor, Dc, κ, and Relative Humidity (Petters et al., 2007). The final calculated CCN number concentration was then derived from SMPS measurements by integrating all particles larger than Dc. The water tension of 0.072 J m-2 was used unless otherwise specified. For the second method, critical activation diameters were derived from size segregated CCN measurements and used similarly to the previous method - integrating all particles larger than Dc to derive the calculated CCN.

Figure 1 shows the CCN activation dependence on aerosol chemical composition with very similar effects in both locations, Southern Ocean as well as North East Atlantic. As expected, sea salt dominated particles displayed the best activation or the smallest critical diameters at the same supersaturations. It was followed by sulphate dominated particles, which activation was pretty similar to laboratory generated ammonium sulphate particles. On average, the activation performance of marine organics was similar in both locations, which points to a comparable biological source or, at least, the source resulting in aerosol of the similar CCN properties. However, the CCN activation of marine organics was better if compared to the anthropogenic organic matter activation (green line versus black in Figure 1, right side). Figure 1 contains only primary marine organics, which good activation into CCN has already been demonstrated (Ovdnevaitė et al., 2011).

Figure 1. Supersaturation and critical CCN activation diameter relationships for distinct chemical composition particles. (Left) Southern Ocean PEGASO cruise (Right) Mace Head atmospheric research station; Slope colours indicate the dominant aerosol compound derived from the pie charts in the upper panel. Three clean aerosol cases for both PEGASO and Mace Head with dominant sulphate (red), sea salt (brown) and organic matter (green) were plotted, in addition one polluted case with dominant anthropogenic organics (black) was added to Mace Head plot. Also, laboratory activation curves for ammonium sulphate (solid grey line) and sea salt (dashed grey line) are presented.

A potential of representing the dichotomous effects by a κ-Kohler theory was evaluated. κ-Kohler theory is one of the most widely used CCN activation theories, which is claimed to be able to provide CCN
concentrations using either chemical aerosol composition or hygroscopicity. It usually works reasonably well in regions dominated by anthropogenic sources yet its suitability for reproducing marine CCN has not been properly investigated.

Similarly, a CCN activation representation by Kohler theory was investigated for organic rich newly formed secondary particles registered at Mace Head. κ-Kohler equation was applied in two ways – using κ calculated from HR-ToF-AMS chemical composition and CCN activity derived from SS vs De equation, obtained from the size segregated CCN measurements. Chemical composition derived κ resulted in a significant underestimation of total CCN particles if compared to the CCNC measurements during the Open Ocean Nucleation events (O'Dowd et al., 2010). Organic matter showed a significant contribution to both ultrafine and accumulation mode particles and its hydrophobic properties resulted in a low number of CCN particles derived from combination of κ-Kohler theory and SMPS size distributions. On the other hand, size segregated CCN indicated a different activity for ultrafine particles if compared to accumulation mode ones. Former possessed smaller critical activation diameters than the latter at the same supersaturations, which resulted in a higher number of CCN derived from ultrafine particles, which, in turn, resulted in a closure between the measured and calculated CCN.

CONCLUSIONS

CCN concentrations were calculated using κ derived from aerosol hygroscopicity measurements and compared to the ambient CCN measurements. The results show that at low super-saturation (0.3%) κ-Kohler tends to underestimate marine CCN concentrations, pointing at primary marine organic effects. However, calculated and measured CCN concentrations are in reasonably good agreement at high super-saturations (1%). This is due to the fact that critical particle activation diameter decreases with increasing super-saturation and that marine organics tend to enhance the size of sea spray particles (Yoon et al., 2007), thereby, the number of particles that haven’t been activated decreases with an increasing super-saturation. Given that models can reproduce this increase in particle size, the remaining discrepancies between the real CCN and predicted by the κ-Kohler could be insignificant for certain super-saturations. On the other hand, secondary marine organics exhibit similar enhancing effect on CCN activation, but require a more sophisticated state of the art thermodynamic model to account for the liquid-liquid phase separation (Zuend et al., 2012) and organic effect of ultrafine particles on CCN activation.

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REFERENCES


SOURCES OF CLOUD CONDENSATION NUCLEI OVER THE REMOTE SOUTHERN OCEAN

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Keywords: CCN, sea spray, hygroscopicity, Southern Ocean.

INTRODUCTION

The Southern Ocean is one of the most pristine regions on earth and one of the cloudiest, it is therefore an important test bed for aerosol cloud interactions. Natural aerosols from regions such as the Southern Ocean substantially contribute to the uncertainty in modelled global aerosol forcing (Carslaw et al., 2013). On a regional scale biases in modelled outgoing shortwave radiation have also been identified over the Southern Ocean, particularly in the summer months, which has been linked to the absence of modelled low to mid-level cloud (Bodas-Salcedo et al., 2012).

The role of aerosol derived from marine biota, a dominant process of marine aerosol production in the summer months, on cloud condensation nuclei and cloud droplet populations is poorly characterised. Marine biota influences the aerosol population through the production of precursor gases, such as dimethyl sulfide, which can play a role in new particle formation and secondary processing of particles. In addition, the organic enrichment of primary sea spray aerosol (SSA) influences their water uptake and CCN capacity. The biogeochemical processes driving aerosol cloud interactions over the Southern Ocean are likely to shift in a changing climate, and therefore understanding the aerosol production mechanisms is essential.

Non-sea salt (nss) sulfates have consistently been identified as the largest contributor to number concentrations over the remote oceans, nucleation in the free troposphere, entrainment into the marine boundary layer and subsequent growth appears the most likely source of nss sulfate CCN. Observations over the remote Pacific Ocean indicate that particles from the free troposphere contribute 65% to the marine boundary layer CCN immediately, and after growth in the marine boundary layer another 25%. Seasonal and spatial variability in cloud droplet number concentrations in the Southern Ocean lower latitudes (35°S - 45°S) has been linked to nss sulfate concentrations (Korhonen, et al., 2008; McCoy et al., 2015).

Sea salt has been observed to contribute 10 to 20 % of the remote marine boundary layer CCN over the Pacific Ocean (Blot et al., 2013; Clarke et al., 2013) and estimated to contribute about 55% to summertime Southern Ocean cloud droplet concentration and 80% in the wintertime (Korhonen et al., 2008; McCoy et al., 2015). Summertime measurements of nascent SSA indicate the presence of an organic fraction made up of components such as polysaccharides, lipids and proteins exuded from algal species. SSA organics are largely comprised of a non-volatile component, making up approximately 90% of the SSA volume (Quinn et al., 2014). The SSA organic fraction has been identified as a driver for CCN and cloud droplet number variability in the Southern Ocean mid latitudes (45°S - 55°S). The mechanism for enhanced cloud droplet concentrations with increased SSA organic fraction is poorly understood. In-situ observations over the Southern Ocean are required to better characterise the CCN sources.
METHODS

In recent years QUT have contributed volatility and water uptake measurements to a number of investigations of remote marine aerosols over the Southern Ocean on-board on Australia’s blue water research vessel, RV-Investigator (Hobart, Australia). These voyages include the Cold-Water Trials of the RV-Investigator in January/February 2015, and the Clouds, Aerosols, Precipitation, Radiation and Atmospheric Composition Over the Southern Ocean (CAPRICORN) project in March/April 2016 (RV-Investigator). Figure 1 shows the tracks for these two voyages.

![Image](image.png)

**Figure 1. Voyage track for the Cold Water Trial of the RV-Investigator and the CAPRICORN projects.**

Instrumentation deployed on each of these voyages included (but was not limited to) a Volatility and Hygroscopicity Tandem Differential Mobility Analyser (VH-TDMA), scanning mobility particle sizers (SMPS), a cloud condensation nuclei counter (CCNc), condensation particle counters (CPC) and an Aerosol Chemical Speciation Monitor (ACSM). A short and long column SMPS were used to measure the size range from 4 to 430 nm and 14 to 700 nm, and the CCNc was set to a constant supersaturation of 0.5%.

The VH-TDMA pre-selects particles of a particular size based on their mobility diameter, conditions them and measures the subsequent particle size distribution using two parallel SMPSs. Humidification and volatilization conditioning are combined in the VH-TDMA to distinguish between components of heterogeneous mixtures, providing valuable information on the composition and mixing state of marine particles (Johnson et al., 2004). In this study 40, 100 and 150 nm particles were pre-selected and exposed to 90% RH. Measurements were alternated between room temperature and 250 °C sampling, providing the hygroscopic growth factor (HGF) of the total ambient aerosol and of the non-volatile fraction.

All VH-TDMA data were inverted using the TDMainv algorithm (Gysel et al., 2009). Particle hygroscopicity was modelled with $\kappa$ values, and the $\kappa$-Köhler method was used to estimate the critical diameter for cloud droplet activation (Petters & Kreidenweis, 2007). Size distributions were subsequently used to estimate CCN concentrations, based on $\kappa$ from each mode in the HGF distribution, and compared with direct CCNc observations. Data have undergone an initial screening for the influence of combustion...
related pollution directly from the ship engines. For example data are limited to wind directions from 97° to 277° relative to the ships bow, and periods with a black carbon concentration of less than 50 ng/m³.

CONCLUSIONS

During the CAPRICORN voyage average particle number concentrations were 353 ± 260 cm⁻³. Particle number concentrations were dominated by a moderately hygroscopic mode (average HGF of 1.5) which was volatile at 250 °C and an externally mixed non-volatile highly hygroscopic mode (average HGF of 1.8). This is consistent with an external mixture of nss sulfates and SSA. In addition, a small contribution from a non-hygroscopic mode was also observed, further investigation is required to determine the source of this mode. On average the SSA mode contributed 32% to the particle number concentration at 100 nm, 12% at 40 nm and 44% at 150 nm (Figure 1). The nss sulfate mode contributed 45 to 73% to the overall number concentrations on average.

![Figure 2. Number fraction of three HGF modes for CAPRICORN voyage. Error bars show ± 1 sd.](image)

The HGF of the SSA mode was suppressed relative to inorganic sea salt, indicating a substantial internally mixed primary organic fraction and/or inorganic sea-salt aging and a secondary organic component. An upper limit for the organic volume fraction (OVF) can be calculated via the Zdanovskii-Stokes-Robinson (ZSR) assumption assuming an internally mixed nascent SSA particle. An artificial sea-salt HGF of 2.35 (Modini et al., 2010) and a HGF for the organic fraction from 1 to 1.5 were used to yield an OVF of 60 to 74%, respectively. No shape correction to the SSA HGF was applied, the large organic fraction is assumed to increase the particle sphericity. Electron microscopy samples collected during the voyage will be analysed for particle morphology and used to constrain the SSA shape factor.

Voyage average CCN concentrations were 95 ± 66 cm⁻³ and CCN concentrations calculated from HGF distribution averaged 112 ± 83 cm⁻³. To estimate CCN from TDMA measurements each peak in the HGF distribution was used i.e. particle mixing state was taken into account. CCN concentrations were also calculated using an average HGF, giving 156 ± 97 cm⁻³. Averaged HGFs produced CCN values that were substantially larger than measured values. This highlights the importance of mixing state, small changes in particle composition, and therefore critical diameter, can lead to relatively large changes in CCN concentration.
Detailed CCN source apportionment for the Cold-Water Trial and CAPRICORN will be presented. These data and those from further Southern Ocean voyages will enhance the process understanding of aerosol-cloud interactions in this region and future modelling efforts.

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REFERENCES


CCN measurements at the Princess Elisabeth Antarctica Research Station

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 Keywords: CCN, hygroscopicity, PSCF, antarctic aerosol.

INTRODUCTION

Aerosol particles play a major role in the energy budget of the earth. They can directly interact with solar radiation via absorption and scattering. But due to their ability to act as Cloud Condensation Nuclei (CCN), they also indirectly interact with solar radiation through modulation of the cloud albedo (Twomey, 1974). For a better understanding of the anthropogenic influence on the earth’s climate knowledge about the natural pre-industrial aerosol background is needed. As Antarctica is located far from anthropogenic activities it is one of the most pristine areas on the globe (Hamilton et al., 2014) and hence a favorable environment for natural aerosol background studies.

For three austral summer seasons (2013-2016, each from December to February) a Condensation Particle Counter (CPC), Cloud Condensation Nucleus counter (CCNc) and a Laser Aerosol Spectrometer (LAS) were operated at the Belgian Antarctic research station Princess Elisabeth to measure the aerosol composition inside the Antarctic boundary layer. With this data set we want to study the variability of the Condensation nuclei (CN) and CCN concentration and identify their sources, sinks and transport pathways and analyze the particle hygroscopicity.

METHODS

Measuring site

The research station Princess Elisabeth, in Dronning Maud Land, East Antarctica (71.95° S, 23.35° E, 1390 m asl.) is a zero emission station and hence excellent for conducting in situ aerosol measurements. It is located upon the granite ridge of Utsteinen Nunatak in the Dronning Maud Land region of East-Antarctica. It approximately has a distance of 220 km from the Antarctic coast and is at an altitude of 1382 meters above the sea level. The station is inhabited from November through end of February and is operated under remote control during the other months.

Instrumentation

The CCN number concentration ($N_{CCN}$) was measured using a Droplet Measurement Technologies (DMT, Boulder USA) Cloud Condensation Nuclei counter (CCNc-100). The CCNc is a continuous-flow thermal-gradient diffusion chamber and is described in detail by Roberts and Nenes (2005). $N_{CCN}$ was measured at five fixed supersaturations (SS, 0.1%, 0.2%, 0.3%, 0.5% and 0.7%). The total particle number concentration ($N_{CN}$) was measured by a Condensation Particle Counter (CPC, TSI model 3776) which has a lower cut off at 3nm and was operated at a total flow rate of 11/m. In parallel the particle number size distribution ($PNSD$) was measured by means of a Laser Aerosol
Spectrometer (LAS-X 3340, TSI) in the size range from 92 nm up to 6.8 µm. In addition to the aerosol instrumentation an automatic weather station and a radiosonde system measured standard meteorological parameters at the ground and lower atmosphere, respectively.

**Hygroscopicity**

In this work, we apply the single-parameter \( \kappa \)-Koehler theory (Petters and Kreidenweis, 2007) to infer the hygroscopicity of the ambient CCN. Therefore \( N_{CCN} \) and the PNSD are used to determine the critical diameter (\( D_c \)) which in combination with the SS at which \( N_{CCN} \) was measured is used to derive the hygroscopicity parameter \( \kappa \).

**Potential Source Contribution Function**

To apply the Potential Source Contribution Function (PSCF), 10-day back trajectories were calculated every hour at 5 different locations (one is starting exactly at the measurement station and 4 in close proximity around it) and at three heights (100m, 200m and 300m). To calculate the PSCF the whole region that is covered by the trajectories is divided into an array of 5x5 degree grid cells (i,j). The approach is that aerosol particles that are emitted in such a cell are incorporated into the air parcel and transported to the receptor site. Therefore the aerosol properties that were measured at the receptor site were matched with the starting time of the trajectories. The PSCF can be calculated as follows:

\[
PSCF_{i,j} = \frac{m_{i,j}}{n_{i,j}},
\]

where \( n_{i,j} \) is the total number of trajectory segment endpoints that fall into a cell and \( m_{i,j} \) is the number of trajectory segment endpoints that fall into a cell and exceed a given criterion value. It is probable that small values of \( n_{i,j} \) would lead to uncertain and high PSCF values. Thus, PSCF values for \( n_{i,j} \) that is below an empirical threshold of 30 segment endpoints per grid, were neglected. According to Hopke *et al.* (2016): “Cells containing emission sources would be identified with conditional probabilities close to 1 if trajectories that have crossed the cells effectively transport the emitted contaminant to the receptor site. The PSCF model thus provides a means to map the source potentials of geographical areas. It does not apportion the contribution of the identified source area to the measured receptor data.”

**RESULTS**

**Particle number concentrations and hygroscopicity**

Table 1 gives an overview concerning the measured concentrations of CN and CCN and the inferred \( \kappa \)-values (seasonal median, 10% percentile and 90% percentile). Generally \( N_{CN} \) is in the order of some hundreds of particles per cm\(^3\). \( N_{CCN} \) covers a range between less than 10 at SS=0.1% and several hundreds of particles per cm\(^3\) for larger supersaturations. Fluctuations in \( N_{CN} \) and \( N_{CCN} \) either seem to occur due to new particle formation (NPF) events or due to precipitation. During NPF events \( N_{CN} \) can reach concentrations of several thousands of particles per cm\(^3\) on a time scale of some hours to one day. NPF events may also result in increased \( N_{CCN} \), however with a certain time delay, indicating particle growth up to sizes that are relevant for cloud droplet activation. Strong precipitation events (5-10 mm/d) imply a significant reduction of \( N_{CCN} \) that could
be due to scavenging. The hygroscopicity can only be inferred for SS=0.1% as for higher SS the critical diameter would fall below the lower diameter limit of the PNSD. $\kappa$ is very variable and ranges between 0.4 and 1.2, which is indicative for different aerosol particle sources and chemical composition. A lower hygroscopicity hints at a larger fraction of organic matter, whereas a larger hygroscopicity can be caused by a larger amount of sulfate or sea salt.

<table>
<thead>
<tr>
<th></th>
<th>13/14</th>
<th>14/15</th>
<th>15/16</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{CN}(CPC)[1/cm^3]$</td>
<td>280.9 (191.9, 634.7)</td>
<td>352.9 (206, 735.9)</td>
<td>340.3 (227.2, 952.3)</td>
</tr>
<tr>
<td>$N_{CN}(LAS)[1/cm^3]$</td>
<td>18 (11.9, 24.2)</td>
<td>-</td>
<td>23.1 (14.8, 36.41)</td>
</tr>
<tr>
<td>$N_{CCN,0.1%}[1/cm^3]$</td>
<td>8.9 (4.2, 13.5)</td>
<td>8.5 (5.5, 13.6)</td>
<td>11.5 (6.8, 24.2)</td>
</tr>
<tr>
<td>$N_{CCN,0.2%}[1/cm^3]$</td>
<td>68.0 (40.4, 96)</td>
<td>79.7 (58.4, 103.4)</td>
<td>83.7 (56.1, 123.6)</td>
</tr>
<tr>
<td>$N_{CCN,0.3%}[1/cm^3]$</td>
<td>97.2 (59.8, 136.9)</td>
<td>122.9 (97.4, 169.3)</td>
<td>130.5 (95.7, 182.1)</td>
</tr>
<tr>
<td>$N_{CCN,0.5%}[1/cm^3]$</td>
<td>130.9 (80, 186.1)</td>
<td>190.7 (141.1, 261.5)</td>
<td>187.9 (140.9, 288.2)</td>
</tr>
<tr>
<td>$N_{CCN,0.7%}[1/cm^3]$</td>
<td>152.8 (93.9, 228.5)</td>
<td>236.8 (161.4, 325.5)</td>
<td>223.8 (165.2, 366)</td>
</tr>
<tr>
<td>Kappa0.1%</td>
<td>0.81 (0.63, 0.97)</td>
<td>-</td>
<td>0.93 (0.78, 1.09)</td>
</tr>
</tbody>
</table>

Table 1: Overview table with median values of CN and CCN number concentrations and kappa values measured at the Antarctic research station Princess Elisabeth. The values of the 10% percentile and the 90% percentile are in brackets.

**PSCF results**

Figure 1 shows the spatial distribution of the PSCF calculated for $N_{CCN,0.7%}$ values that exceed the 75% percentile ($\geq 465$ particles per $cm^3$). The analysis was done using the data of all three austral summer periods, which are approximately 230 days and a corresponding set of 88000 back trajectories. The map indicates which areas have a high potential to contribute to high $N_{CCN,0.7%}$ values measured at the receptor site. It seems that the marine area between 40°S and 60°S contributes most to high particle concentrations. A high density of storms with high wind velocities are typical for this area and might lead to a significant production of sea spray. However the Antarctic continent does not represent an area that contributes to high CCN concentrations. Furthermore figure 1 indicates that the CCNs are mainly originating from natural sources as the 10-day back trajectories do not cover continental areas (except of Antarctica) or areas that are anthropogenically influenced.

**CONCLUSION AND OUTLOOK**

The here presented data set is, to our knowledge, the most comprehensive set of CCN measurements in East-Antarctica. It shows that fluctuations in number concentrations of CN and CCN are mainly driven by either new particle formation or scavenging due to precipitation. The hygroscopicity for particles that are larger as 100nm was found to fluctuate around $\kappa$ values of 0.9. Back trajectories and their application in the PSCF model indicate that the marine area around Antarctica (up to 40°S) has a high probability to be the origin of high CCN concentrations. Furthermore the Concentration Weighted Trajectory (CWT) analysis and a clustering analysis is planned. Also a more detailed analysis of the data set in combination with additional available data still needs to be done.
ACKNOWLEDGEMENTS

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REFERENCES


GLOBAL TRENDS OF CLOUD CONDENSATION NUCLEI CONCENTRATIONS

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Keywords: AEROCOL-CLIMATE INTERACTIONS, CCN, CLIMATE MODEL.

INTRODUCTION

Atmospheric aerosols can influence cloud optical and dynamical processes by acting as cloud condensation nuclei (CCN). Globally, these indirect aerosol effects are significant to the radiative budget as well as a source of high uncertainty in anthropogenic radiative forcing (IPCC, 2013). While historically many global climate models have fixed CCN concentrations to a certain level, most state-of-the-art models calculate aerosol-cloud interactions with sophisticated methodologies based on interactively simulated aerosol size distributions (Ekman, 2014). However, due to scarcity of atmospheric observations simulated global CCN concentrations remain poorly constrained. Here we assess global CCN variability with a climate model, and attribute potential trends during 2000-2010 to changes in emissions and meteorological fields.

METHODS

ECHAM5-HAM (Stier et al., 2005) is an aerosol-climate model originally developed at Max Planck Institute, Hamburg. The model has been actively involved in model intercomparison studies, such as CMIP. The host model ECHAM and aerosol model HAM are part of a large family of models comprising the Earth System Model MPI-ESM. This allows flexible combinations of several model components for different needs. Available components are for example land-vegetation model JSBACH, ocean model MPI-OM and ocean biogeochemistry model HAMOCC. The aerosol module HAM includes two options for the aerosol microphysics model, M7 and SALSA.

Here we have used ECHAM5.5-HAM2 with model M7 microphysical aerosol model (Zhang et al., 2012). The model has been upgraded with a secondary organic aerosol (SOA) scheme including ELVOCs (Jokinen et al., 2015). Dust and sea salt emissions are calculated online, based on wind speed and hydrology. We calculate CCN at 0.2% supersaturation from the aerosol size distribution. The four experiments carried out are listed in Table 1. Each experiment is 11 years, analysed after a 6-month spin-up period. The MODIS CCN product (Terra platform) is used to evaluate model performance throughout 2000-2010. While passive optical remote observation of CCN could include deficiencies (e.g. Shinozuka et al., 2015), the product serves as a proxy for changes during the simulation period. In our analysis we utilize the observed and simulated vertical column integrated CCN concentration (cm⁻²), and limit our analysis only over marine regions.

<table>
<thead>
<tr>
<th></th>
<th>Emission</th>
<th>Meteorology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>ACCMIP</td>
<td>Nudged</td>
</tr>
<tr>
<td>FixedEmis</td>
<td>Climatological 2000-2010</td>
<td>Nudged</td>
</tr>
<tr>
<td>FixedMeteo</td>
<td>ACCMIP</td>
<td>Fixed 2010</td>
</tr>
<tr>
<td>DecrEmis20</td>
<td>ACCMIP+20% decr. 2009-2010</td>
<td>Nudged</td>
</tr>
</tbody>
</table>

Table 1. Experimental design. Nudging refers to assimilating model meteorology towards reanalysis fields of ERA-Interim dataset.
RESULTS

Simulated annual CCN column densities (not shown) reach $2 \times 10^8$ cm$^{-2}$ near strong source regions in central Africa, Arabian Sea, Bay of Bengal, and China Sea. The concentration gradient in CCN(0.2%) is steep, and column densities drop to <50% a few hundred kilometers away from the coasts. While the spatial distribution of CCN at 0.2% supersaturation is closer to that of MODIS proxy, as opposed to 1.0% supersaturation, the overall column integrated CCN are too low. Still, we can compare the relative response of CCN to emission and meteorological variability. Figure 1 shows the correlation of annual-average CCN from MODIS and ECHAM-HAM during 2000-2010. Most evident pattern of high correlation is found over North Atlantic Ocean, extending throughout Europe and up to Gulf of Mexico. All of these regions show a generally decreasing trend throughout the decade in simulations (Control) and MODIS CCN, and the simulations including the emission trends clearly improve the simulations with climatological emissions (FixedEmis). In regions where the observed intra-annual cycle correlates well with sea-spray emissions (Figure 1), the long-term annual correlation usually remains poor. This could indicate that the model is unable to capture the natural variability in aerosol emissions.

Figure 2 shows the simulated trends in CCN(0.2%) during 2001-2010. The CCN over North America shows a declining trend throughout seasons, caused by both decreasing anthropogenic emissions (FixedMeteo) and decrease in natural background CCN (FixedEmis). While western Europe shows a
significant decrease specifically during summer months, the eastern sector indicates some CCN increase
due to changes in natural emissions. In Eastern China, simulated natural CCN formation seems to
decrease, while anthropogenic perturbations cause a positive trend of a few percent per year. The
simulated trends are in good agreement with MODIS data around North America, Europe and Eastern
Siberian outflow. However, the MODIS CCN decrease over outflow from China cannot be fully captured
in model simulations. The model experiments allow to isolate CCN variability and trends caused by
anthropogenic and natural emissions, as well as meteorological conditions.

ACKNOWLEDGEMENTS

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REFERENCES

Ekman, A. (2014). Do sophisticated parameterizations of aerosol-cloud interactions in CMIP5 models
IPCC Climate Change 2013: The Physical Science Basis (eds Stocker, T. F. et al.) (Cambridge Univ. Press,
2013).
Jokinen, T. et al. (2015): Production of extremely low-volatile organic compounds from biogenic
emissions: Measured yields and atmospheric implications, P. Natl. Acad. Sci. USA, 112, 7123–7128,
doi:10.1073/pnas.1423977112.
Shinozuka, Y., et al.: The relationship between cloud condensation nuclei (CCN) concentration and light
extinction of dried particles: indications of underlying aerosol processes and implications for satellite-
improvements in process representations, Atmos. Chem. Phys. 12, 8911-8949, doi:10.5194/acp-12-
8911-2012.
CLIMATE ENGINEERING BY ARCTIC WINTER CIRRUS THINNING: RISKS AND FEASIBILITY

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Keywords: Climate Engineering, Arctic Cirrus, Nucleation, Aircraft.

INTRODUCTION

Climate Engineering (CE) aims at counteracting anthropogenic caused global warming by pointedly interceding in the climate system. (Caldeira et al., 2013; Keith, 2000). Various theoretical approaches exist, e.g. artificially removing carbon dioxide (Carbon Dioxide Removal) or manipulating solar radiation fluxes (Solar Radiation Management, SRM) (Sheperd, 2012). One method within the scope of SRM is thinning of cirrus clouds (Mitchell and Finnegan, 2009). Here, the warming effect of these clouds is reduced as the longwave emission into space is enhanced. Cirrus are ice clouds that develop usually at temperatures lower than 235 K. Regarding their radiation balance, the warming effect due to backscattering of outgoing longwave radiation dominates the cooling effect caused by scattering of shortwave radiation (Lohmann et al., 2008). Therefore, by reducing both the frequency of coverage as well as the life time of these clouds by seeding these clouds with ice nucleating particles (INP), global cooling may be achieved. In the winter hemisphere and here particularly in the Polar Regions, the method is most efficient as the counteracting shortwave radiation is not present due to the polar night (Storelvo et al., 2013). This is an advantage of arctic winter cirrus thinning (AWiCiT) compared to global thinning or other methods of SRM that mostly aim modifying shortwave radiation, including all side effects associated. Exploiting the strong polar sea-ice-albedo feedback (Holland and Bitz, 2003) makes AWiCiT most efficient. Furthermore, the method operates in a very sensitive region, where e. g. the Greenland ice sheets or methane retaining permafrost soils. Negative changes here may cause potential irreversible tipping points regarding climate change (Smith et al., 2009).

Within this project, following questions are considered: Is AWiCiT feasible and how much cooling can be achieved at maximum? Risks and side effects of AWiCiT include impacts on the polar vortex, the arctic stratosphere and the ozone layer as well as changes in the lower lying clouds.

METHODS

To quantify the effects of AWiCiT on the regional scale, the online coupled weather forecast and chemistry model ICON-ART (Rieger et al., 2015) is used. The focus of this study lies on an episode of five day in January 2016. Exploiting the two-way nesting capabilities of ICON-ART, in global simulations with a horizontal resolution of approximately 40 km, areas with local refinements over the arctic region down to 2.5 km are placed. Up till now, modeling studies of AWiCiT with such high spatial resolution and the advantages that rise therewith in terms if accuracy and complexness of the processes reproduced are not published yet.

To simulate aerosol-cloud-interaction, the comprehensive two-moment microphysical scheme of Seifert and Beheng (2006) is applied. The impact on radiation is calculated using a diagnostic radiation scheme (Mlawer et al., 1997).

The influence of the seeding aerosol on the development of cirrus clouds depends from the fraction of homogeneous nucleating particles as well as on the concentration of preexisting INP. Therefore, the
spatial and temporal distribution of both anthropogenic as well natural INP determines the efficacy of AWiCiT.

In the simulations, seeding aerosol is emitted via commercial long distance flights over the arctic region. Information on flight tracks are available with very high spatially and temporally resolved real time flight tracks (flightradar24.com, 2016). The dilution of the initial concentration of the seeding aerosol depends on wind shear (Dürbeck and Gerz, 1996).

To calculate the nucleation of cirrus ice crystals, the parameterizations after Barahona and Nenes (2008; 2009) are applied. An artificial species with a freezing threshold like Bismut(III)-iodid (BiI3) is assumed here, as BiI3 is thought to be a promising ice nucleating aerosol (Mitchell and Finnegan, 2009).

CONCLUSIONS

Work is still in progress; therefore, all of the results are only preliminary yet. Nevertheless, first conclusions can be drawn.

A crucial first step of this project is validation of the model. Thinning of cirrus clouds can only be effective, when natural cirrus develops primarily from homogeneous freezing of solution droplets. In case that these clouds evolve mainly from heterogeneous nucleation, seeding would lead to warming instead of the cooling desired (Cziczo et al., 2013).

Reference simulations without considering seeding but including transport and activation of mineral dust and anthropogenic emissions are carried out. Comparison of simulations and CALIPSO data (Winker et al., 2009) for cirrus clouds in terms of frequency of occurrence and spatial distribution as well as regarding their microphysical properties show good agreement. Apparently, cirrus clouds over wintertime arctic regions in the simulated situation consist mainly of ice crystals evolved from homogeneous nucleation. Therefore, seeding can have the desired impact of creating few but larger ice crystals.

Analyzing the temporal and spatial evolution of the concentrations of seeding aerosol emitted along commercial flight tracks show a homogeneous distribution of the particles after a few days. Here, despite no aircrafts pass the higher polar region, the polar vortex is capable to transport the aerosol further north. The concentration of INP available has strong impact on AWiCiT. Too few particles have no impact as they cannot effectively suppress homogeneous nucleation. Therefore, cirrus clouds remain unaffected by seeding. In contrast, too many particles suppress homogeneous nucleation but here, more ice crystals evolve from seeding than would have nucleated homogeneously without it. These artificial cirrus clouds than in turn have a net warming effect.

Sensitivity studies with variable initial concentrations were carried out to determine the optimal amount of aerosol for achieving the maximum reduction of cirrus clouds by creating the largest mean crystal diameters possible without over-seeding. For the artificial BiI3 aerosol, seeding INP concentrations between 50 l\(^{-1}\) and 100 l\(^{-1}\) have the largest impact. This is comparable to the results of studies using climate models (Storelvmo et al., 2013).

REFERENCES


Barahona D, and A. Nenes (2009). Parameterizing the competition between homogeneous and heterogeneous freezing in cirrus cloud formation - monodisperse ice nuclei, Atmos. Chem. Phys. 9, 369 - 381.


ACCUMULATION MODE FROM CLOUD PROCESSING

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Keywords: AEROSOL, ACCUMULATION MODE, CLOUD PROCESSING.

INTRODUCTION

Surface aerosol size distributions from a Scanning Mobility Particle Sizer (SMPS) and remote sensing by a ceilometer (CEIL), Total Sky Imager (TSI) and pyranometer gridded network (PGN) were used to investigate cloud processing at the Oklahoma Department of Energy Southern Great Plains Atmospheric Radiation Measurement site in May, 2003 (Gasparini et al., 2006). Chemical transformations within cloud droplets, coalescence among droplets and Brownian capture of interstitial material by cloud droplets make bimodal aerosol because these processes increase material within droplets. When droplets evaporate, as they usually do, their residuals are larger than particles that did not nucleate cloud droplets. This resulting bimodality is characteristic of cloud processing. This is usually manifested in a size gap because critical supersaturation, $S_c$, is generally inversely related to size. These two modes are then separated by a concentration minimum at a size referred to as the “Hoppel minimum.” These modes are cloud processed (accumulation) and cloud unprocessed (Aitken) (e.g., Hudson et al., 2015; hereafter H15). Particles that remain within the Aitken mode after cloud processing are unaltered, but the Aitken mode is altered by removal of larger or more cloud-active (low $S_c$) particles. Accumulation mode particles are not created by cloud processing; they are rather transferred from the Aitken mode.

While much discussion on cloud processing has focused on marine clouds and particles, cloud processing has also been observed in continental environments; i.e., central USA (Hoffmann, 1993); Germany (Birmili et al., 2001); and Nordic background (Tunved et al., 2003). All of these studies cited cloud processing as the reason for aerosol bimodality.

METHODS

Instead of the subjective categorization of aerosol modality used by H15 we now use the concentrations within the two modes; Aitken (unprocessed), $N_p$, and accumulation (processed), $N_a$. $N_a - N_p$ is then an objective measure of particle modality. Higher values indicate unimodal aerosol while lower $N_a - N_p$ indicate bimodal aerosol. $N_a - N_p$ can be normalized by dividing by $N_a + N_p$.

FINDINGS

Figure 1A and B show high correlations between mean hourly diameters of the two modes and Hoppel minima, which can only result from a process that simultaneously affects both modes. Other processes are responsible for some of the particles within the two modes. But no other processes are known to simultaneously affect both modes in this coordinated fashion. Non-cloud processes would impart separate effects to each mode. Figure 1C demonstrates the large size separation between the modes and of the two modes from Hoppel minima between them.

Correlation coefficients, $R$, of aerosol modalities with cloud base altitude (CBA) and cloud fraction (CF) are presented in Fig. 2. Lower CBA and higher CF should enhance surface aerosol bimodality. Since bimodality is denoted by lower values it ought to positively correlate with CBA and negatively correlate with CF. The CF R signs are therefore reversed/negated in order to positively demonstrate cloud processing. Time differences between the instantaneous remote cloud measurements and subsequent
Figure 1. Relationships between hourly mean diameters of (a) processed/accumulation mode and unprocessed/Aitken mode, (b) Hoppel minima and accumulation mode. Blue coefficients of determination exclude the 3 outlying data, which reduces data from 428 to 425. All two-tailed probabilities are < 10⁻⁴. (c) Mean diurnal trends for mean diameters of SMPS modes and Hoppel minima between modes.

Figure 2. Correlation coefficients (R) between hour averages of SMPS modality with CEIL cloud base altitude (CBA) and cloud fraction (CF) and TSI and PGN CF against time lag of aerosol after cloud. Sign reversal for CF Rs.

Surface aerosol responses after advection of cloud-altitude aerosol are accounted for by time-lagging the aerosol measurements. This provides R of cloud measurements with later surface aerosol measurements (positive lags). R is low for negative (aerosol prior to the specific cloud measurements) or zero lag (simultaneous aerosol and cloud measurements) and positive for small positive aerosol lags. Further aerosol lags show declining R. Air motion variations during the 21-day measurement period evoke time-lag variations that spread positive R over several lag hours. Plots similar to Fig. 2 for each day of this project showed higher Rs as revealed by the mean Rs in Table 1. Even these higher Rs are downgraded by variations of aerosol lags within some of these 24-hour periods. R values for each of the three different “periods” of Table 1 (21 days, mean of daily means and with 5-hour running means) are in the order of the sky coverage of the three instruments. CEIL with just a vertical line of coverage always has the lowest Rs while PGN with the largest sky coverage (nearly equal to Oklahoma) always has the highest Rs.

Mean lags of the various days are inversely related to wind speeds both at the surface and aloft; higher winds make shorter aerosol modality lags to cloud variations. Mean daily aerosol lags are also inversely related to mean daily CF of all 3 instruments in the order of their sky coverage; i.e., PGN has the highest such R. Thus greater CF makes shorter lags. Double regression of PGN CF and wind speed predicts nearly half of the variations of mean daily lags of surface aerosol modality to cloud changes.
<table>
<thead>
<tr>
<th>Inst</th>
<th>Period</th>
<th>N</th>
<th>R</th>
<th>lag</th>
<th>P2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEIL</td>
<td>21 days</td>
<td>383</td>
<td>0.23</td>
<td>7</td>
<td>3.81(-6)</td>
</tr>
<tr>
<td>TSI</td>
<td>21 days</td>
<td>274</td>
<td>0.38</td>
<td>7</td>
<td>1.00(-8)</td>
</tr>
<tr>
<td>PGN</td>
<td>21 days</td>
<td>244</td>
<td>0.44</td>
<td>8</td>
<td>1.00(-8)</td>
</tr>
<tr>
<td>CEIL</td>
<td>mean of 20 daily means</td>
<td>19.3</td>
<td>0.51</td>
<td>9.45</td>
<td>8.80(-2)</td>
</tr>
<tr>
<td>CEIL</td>
<td>mean of 20 daily means; 5-hour running mean</td>
<td>18.4</td>
<td>0.67</td>
<td>10.6</td>
<td>3.37(-2)</td>
</tr>
<tr>
<td>TSI</td>
<td>mean of 21 daily means</td>
<td>12.0</td>
<td>0.73</td>
<td>13.3</td>
<td>3.81(-2)</td>
</tr>
<tr>
<td>TSI</td>
<td>mean of 21 daily means; 5-hour running mean</td>
<td>12.8</td>
<td>0.79</td>
<td>9.8</td>
<td>4.33(-2)</td>
</tr>
<tr>
<td>PGN</td>
<td>mean of 21 daily means</td>
<td>11.5</td>
<td>0.82</td>
<td>10.8</td>
<td>2.43(-2)</td>
</tr>
<tr>
<td>PGN</td>
<td>mean of 21 daily means; 5-hour running mean</td>
<td>8.4</td>
<td>0.88</td>
<td>10.7</td>
<td>1.49(-2)</td>
</tr>
</tbody>
</table>

Table 1. First 3 rows characterize peak Rs in Fig. 3. N is the number of lag is the hour of peak R. P2 is the two-tailed probability. Next 6 rows characterize mean values of peak Rs of daily regressions. Rows 5, 7 and 9 use 5-hour running means of the cloud measurements.

Figure 3A-D displays mean values of aerosol modality as a function of aerosol measurement time lags of specific cloud measurements. For all panels of Fig. 3 the cloud measurements were partitioned into four groups that represent various degrees of potential cloud effects on particles. For the sake of clarity and simplicity only the two extreme quartiles are displayed in each panel. Lowest CBA and greatest CF groups, which should have the greatest potentials toward particle bimodality, are shown in black circles. Highest CBA and smallest CF are the red squares. In panels A-D the black data shifts toward lower modalities (more bimodal) from zero cloud hour toward the hours of maximum Rs in the corresponding plots of Fig. 2. In panels A-D the red data shifts toward higher modalities (more unimodal).

Figure 3E-F demonstrates that the diverse aerosol responses to CF apply to both modes of the particle size distributions in manners consistent with cloud processing. In Fig. 3E the black plot shows \(N_a\) (accumulation mode) increasing in response to the greatest CF quartile whereas the red plot shows \(N_a\) decreasing in response to small CF. By contrast, the black plot for \(N_a\) (Aitken mode) in the F panel decreases in response to greater CF whereas the red plot shows \(N_a\) increases in response to lower CF.

Figure 4 shows that the mean sizes of both aerosol modes and Hoppel minima respond similarly to cloudiness. Higher CF (and lower CBA; not shown) tend to reduce the mean modal sizes in Fig. 4A.
whereas lower CF (and higher CBA; not shown) lead to greater mean modal particle sizes. Since cloud processing would move the larger of the Aitken particles to the accumulation mode this would reduce the mean size of the remaining yet unprocessed Aitken mode. Promotion of these marginal particles would occur to the smaller sizes of the accumulation mode compared to the preexisting accumulation mode particles. This then reduces the mean size of the accumulation mode. Apparently any tendency of the preexisting accumulation mode particles to grow larger by further cloud processing is less than the effect of newly promoted Aitken particles to the low end of the accumulation mode. The opposite size tendencies for \( CF = 0 \) happens when air that has seen less cloud processing advects into the area when clouds disappear (Fig. 4B). The fact that the size tendencies are the same for both modes and Hoppel minima is consistent with Fig 1A.

Figure 4. As Fig. 3 except showing mean diameters of the two modes and Hoppel minima lagged response to extreme CEIL CF.

CONCLUSIONS

In central Oklahoma clouds produce bimodal aerosol spectra even at the surface. This means that most of the accumulation mode results from cloud processing of aerosol.

ACKNOWLEDGEMENTS

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REFERENCES


AEROSOL EFFECT ON WARM CLOUD PROPERTIES OVER CENTRAL INDO-GANGETIC BASIN

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Keywords: CLOUD EFFECTIVE RADIUS, LIQUID WATER PATH, AEROSOL OPTICAL DEPTH

INTRODUCTION

Clouds are one of the major factors that influence the Earth’s radiation budget and also change the precipitation pattern (Altaratz et al 2014, Boucher et al., 2013). Atmospheric aerosols play a crucial role in modifying the cloud properties acting as cloud condensation nuclei (CCN) which increase the cloud droplet concentration, limit cloud droplet size and hence increase cloud albedo (Andreae et al., 2009). Due to the lack of sufficient in situ measurements, the satellite measurements provide a better platform to investigate the relationship between aerosol and cloud properties on a global scale (Huang et al., 2006). In this study, we investigate the influence of aerosols on warm cloud properties (which are mainly in liquid phase) over central Indo – Gangetic Basin (IGB) ranging from region 23° – 28° N and 81° – 86° E, which is also one of the most polluted regions of IGB.

DATA AND METHODOLOGY

In the present study, MODerate resolution Imaging Spectroradiometer (MODIS) on board Terra satellite, level 3, version 6 at a latitude – longitude resolution of 1° x 1° data is used for monsoon season (JJAS) for the period of ten years (2001 – 2010). This decade experienced normal/excess monsoon years and drought which provide an opportunity to understand the relationship between aerosol and cloud properties. We use the daily mean aerosol optical depth (AOD), cloud effective radius (CER) and liquid water path (LWP) for all 25 grid points (5° x 5°). We use only those days data, on which days AOD at 550 nm is less or equal to unity because AOD value greater than unity would have resulted most likely due to cloud contamination (Ramachandran and Cherian, 2008).

RESULTS AND DISCUSSION

IGB is highly polluted, populated and one of the largest river basins, in the world which experience a high aerosol loading throughout the year and also show significant seasonal variation. Annual mean climatology of ten years (2001 – 2010) clearly shows a high aerosol loading over IGB (Figure 1 (a)). The rectangular box represents the region of interest of the present study. LWP and COT are the two-crucial cloud parameters which are linearly dependent on each other (Figure1 (b)). The correlation between LWP and COT as a function of AOD (Figure 1(b)) is found to be high and positive (r = 0.95). Cloud effective radius (CER) is crucial to understand cloud formation, interactions and also provide information about the moisture content of cloud and precipitation intensity (Kubar et al., 2009). In contrast, large variation in CER and LWP is observed (Figure 1 (c)). This is consistent with the recent study by Cheng et al. (2017) who reported a poor correlation between CER and AOD over northern China during summer season. It is observed that higher AOD (>0.8) have maximum liquid water path (Figure 1(c)).
Figure 1. (a) Annual mean AOD climatology (2001 – 2010) over Indian subcontinent, (b) correlation between LWP and COT as a function of AOD and (c) scatter plot between CER (μm) and LWP (g/m²) as a function of AOD during the study period.

CONCLUSIONS

In the present study impact of atmospheric aerosol on warm clouds properties is investigated over IGB. A good correlation between LWP and COT is observed which does not show any significant correlation with AOD. The results from the present study will be important in understating the spatial variation in aerosol – cloud interaction over IGB. Further details will be presented.

ACKNOWLEDGEMENTS

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REFERENCES


SESSION 6:
PARTICLE PHASE CHANGE

Sarah Petters: Temperature- and humidity-dependent phase states of secondary organic aerosols

Ricky Nellas: Thermophysical properties of normal and branched alkanes from nucleation simulations

Murray Johnston: Impact of particle phase chemistry on nanoparticle composition and growth rate
TEMPERATURE- AND HUMIDITY-DEPENDENT PHASE STATES OF SECONDARY ORGANIC AEROSOLS

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Keywords: aerosol phase, aerosol viscosity, secondary organic aerosol, temperature dependence.

INTRODUCTION

Atmospheric aerosols can impact climate and weather processes, visibility and air quality, and human health and wellbeing. The environmental impact of aerosols depends on the number concentration, size distribution, and physicochemical properties of the particles. Secondary organic aerosols (SOAs) form in situ as volatile organic compounds are oxidized and a subset of their reaction products condense into the particle phase. For viscous semi-solid particles the growth and rate of chemical transformation may be limited by molecular diffusion timescales as new material condenses onto a growing particle or as oxidation occurs at the particle surface. Secondary organic aerosols can exist in amorphous semi-solid or glassy phase states whose viscosity varies with atmospheric temperature and relative humidity. However, a dearth of viscosity data for SOA systems limits our understanding of aerosol phase states in the atmosphere. Here we report the viscosities and glass transition temperatures of SOAs as a function of relative humidity and temperature.

METHODS

Secondary organic aerosols were generated by reacting a series of monoterpenes with ozone in a continuous-flow tube reactor in the absence of light. Online measurements of monodisperse aerosol viscosity were performed following the method of Rothfuss and Petters (2016). Briefly, dimers were prepared by coagulation and were then isolated from the population by electrostatic filtration. Viscosity was obtained from the temperature and relative humidity at which semi-solid dimerized particles partially relax into a sphere. Glass transition temperatures were obtained by extrapolating the temperature-dependent viscosity in the range of measurement to 10¹² Pas (Rothfuss and Petters, 2017b). Common functional groups comprising SOA were obtained by derivitizing SOA filter extracts and analyzing the derivatives using spectrophotometry (Aimanant and Ziemann, 2013). The molecular oxygen-to-carbon (O:C) ratio was also estimated using parametrizations of mass spectra from Aerosol Chemical Speciation Monitor (ACSM, Ng et al., 2011).
SUMMARY

Viscosity and glass transition temperatures are related to the measured functional group composition and the O:C ratio of the SOA systems. Results are compared to expectations from functional group models of organic aerosol viscosity (Rothfuss and Petters, 2017a). The temperature-dependent viscosity data are also used with humidity-dependent viscosity data, aerosol hygroscopicity, a Vogel-Fulcher-Tammann temperature dependence model, and the Gordon-Taylor mixing rule to construct a phase state model for SOA.

ACKNOWLEDGEMENTS

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REFERENCES


THERMOPHYSICAL PROPERTIES OF NORMAL AND BRANCHED ALKANES FROM NUCLEATION SIMULATIONS

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Keywords: classical nucleation theory, aggregation-volume-bias Monte Carlo, umbrella sampling, surface tension, omega.

INTRODUCTION

Petroleum fluids are composed of a complex mixture of hydrocarbons and other volatile substances. Recovery and refinery of these industrial fluids involve a plethora of processes, and uncontrolled condensation of these volatile substances would have a very costly impact in the industry (Luijten et. al., 1998). Accurate estimates of thermophysical properties (e.g. surface tension values) of these compounds are crucial in the development of efficient methods in petroleum recovery and refinery (Luijten et. al., 1998; Smit et. al., 1995).

Nucleation is an important part of phase transitions occurring in various processes, ranging from aerosol formation, gas condensation, bubble formation of liquids, crystallization of solids, and nuclear level transitions in matter and the early universe (Nellas et. al., 2010; Chen et. al., 2001; Chen et. al., 2008). In this process, an initial nucleus is formed upon overcoming an activation barrier in cluster formation, depending on experimental temperature and pressure conditions (Chen et. al., 2008; Chen et. al., 2001). Computer simulations have been developed in an attempt to mimic experimental nucleation conditions in a theoretical environment (Chen et. al., 2008; Laaksonen et. al., 1995; Chen et. al., 2001; Smit et. al., 1995). With unprecedented computer power and smart algorithms, nucleation rates and thermophysical properties of clusters can be predicted through nucleation simulations and the use of advanced theoretical formulations such as the CNT and the dynamical nucleation theory (DNT), among others (Kathmann et. al., 2009).

The CNT has been the dominant model in understanding nucleation. While it generally predicts erroneous nucleation rates and critical supersaturations at extreme temperatures, CNT predictions for most gases have been within reasonable error (Laaksonen et. al., 1995). From the CNT equation, thermophysical properties such as surface tension and density may be estimated. As such, this work aims to compute indirectly the surface tension of various alkanes through computer simulations at different temperatures.

METHODS

The nucleation simulations in this work were done using an advance Monte Carlo sampling technique coined as AVUS (Chen et. al., 2001; Nellas et. al., 2010; Kathmann et. al., 2009), aggregation-volume-bias Monte Carlo (AVBMC) with umbrella sampling (US). AVBMC enhances diffusion between phases by employing direct swap moves between the monomer and cluster phases (Chen et. al., 2001; Chen et. al., 2008) while self-consistent US uses a biasing potential to enhance cluster frequencies. AVUS has been proven to efficiently sample rare events such as the gas-to-liquid
nucleation of multicomponent systems (Chen et. al., 2001; Chen et. al., 2008; Nellas et. al., 2006; Nellas et. al., 2008).

The TraPPE-UA (Martin and Siepmann, 1998) force field was used to model all the alkanes. The TraPPE-UA model is one of the most accurate models currently available, predicting saturated liquid densities and critical constants for n-alkanes within experimental error. We employed an energy-based Stillinger-type cluster criterion (Nellas et. al., 2010) for these chain molecules. Based on this criterion, a cluster is defined as a group of molecules of which every molecule has at least one neighbor with an interaction energy of less than \( U_{\text{cl}} = -260 k_B \). For data convergence, each cluster size was sampled for an average of at least \( 10^6 \) times. In this work, the grand-canonical version of the nucleation algorithm was employed (Chen et. al., 2001). The nucleation free energy data was evaluated for all clusters of interest.

**DISCUSSION**

According to the Classical Nucleation Theory, the cluster’s free energy, \( \Delta G(r) \), of formation as a function of the cluster radius contains the surface and bulk free energy contributions (Merikanto et. al., 2007; Nellas et. al., 2010) of the form,

\[
\Delta G(r) = 4\pi r^2 \sigma + \frac{4}{3} \pi r^3 \rho \Delta \mu. \quad (1)
\]

In terms of cluster size \( n \), the cluster’s free energy of formation \( \Delta G(n) \) is

\[
\Delta G(n) = 4\pi \left( \frac{3}{4\pi} \right)^{2/3} \left( \frac{\sigma}{\rho^{2/3}} \right) n^{2/3} + n \Delta \mu. \quad (2)
\]

Using equation (2), the properties of finite-sized clusters can be extrapolated:

\[
\delta \Delta G(n) = \Delta G(n) - \Delta G(n - 1) \quad (3)
\]

\[
\delta \Delta G(n) = 4\pi \left( \frac{3}{4\pi} \right)^{2/3} \left( \frac{\sigma}{\rho^{2/3}} \right) \left[ n^{2/3} - (n - 1)^{2/3} \right] + [n - (n - 1)] \Delta \mu \quad (4)
\]

\[
\delta \Delta G(n) = 4\pi \left( \frac{3}{4\pi} \right)^{2/3} \left( \frac{\sigma}{\rho^{2/3}} \right) [n^{2/3} - (n - 1)^{2/3}] + \Delta \mu \quad (5)
\]

The slope \( m_s = 4\pi \left( \frac{3}{4\pi} \right)^{2/3} \frac{\sigma}{\rho^{2/3}} \) is simplified to 4.836 \( \Omega \), where \( \Omega \equiv \frac{\rho^{2/3}}{\sigma} \).

For this work, the omega values for the normal and branched alkanes are calculated from Figures 1 and 2, respectively.

Figure 1: \( \delta \Delta G(n) \) for normal alkanes as a function of the number of molecules \( n \) at 300 K. From the slopes, characteristic \( \Omega \) values are obtained, from which the surface tension may be calculated.
Figure 2: $\delta \Delta G(n)$ for branched alkanes as a function of the number of molecules $n$ at 300 K. From the slopes, characteristic $\Omega$ values are obtained, from which the surface tension may be calculated.

Existing data on surface tension and density were obtained from Yaws et. al. (Yaws and Pike, 2008). Experimental omega values were calculated from the said data. Agreement between the omega values obtained from simulations and experiments are shown in Figures 3 and 4 for normal and branched alkanes, respectively.

CONCLUSIONS

Nucleation simulations have been done on $n$-alkanes (propane, $n$-butane, $n$-pentane, $n$-hexane, $n$-heptane, $n$-octane, $n$-nonane, $n$-decane, $n$-undecane, $n$-dodecane) and branched alkanes (methylpropane, dimethylpropane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, and 2,2,3,3-tetramethylbutane) modeled using the TraPPE-UA force fields. A simple procedure was developed in determining the omega values of alkanes. From these omega values, surface tension may be obtained without resorting to normal experimental procedures. Investigations as to the applicability of the devised protocol to other classes of compounds are also being conducted.
ACKNOWLEDGEMENTS

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REFERENCES


IMPACT OF PARTICLE PHASE CHEMISTRY ON NANOPARTICLE COMPOSITION AND GROWTH RATE

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Keywords: accretion reactions, biogenic secondary organic aerosol, siloxane secondary aerosol, particle growth model.

INTRODUCTION

The probability that a newly formed particle in the atmosphere ultimately serves as a cloud condensation nucleus (CCN) depends on the rate and mechanism of particle growth. The growth rate must exceed the loss rate in order to reach a climatically relevant size, and the mechanism by which the particle grows affects its chemical composition, morphology and therefore CCN activity. Small nanoparticles grow primarily by condensation of non-volatile compounds. Processes limited by the amount of available surface area, such as condensation, are favoured in small particles where the surface-to-volume ratio is high. Particle phase chemistry has the potential to grow larger nanoparticles if it involves the reaction of semi-volatile reactants to form non-volatile products. Molecular partitioning from the gas phase to the particle phase provides a continuous source of reactant molecules to feed the reaction as it proceeds. Processes limited by the amount of available volume, such as particle phase chemistry, are favoured in larger particles where the surface-to-volume ratio is low. This study assesses the impact of particle phase chemistry, specifically accretion reactions in biogenic and siloxane secondary aerosol, on nanoparticle growth and composition through a combination of experimental measurements and kinetic modelling. The results show that particle phase chemistry can substantially impact the composition and growth rate of particles in the 20-100 nm size range.

METHODS

Nanoparticle formation and growth are performed with a flow tube reactor. Reactants are fed into the flow tube where the point of mixing determines the reaction time. Particles exiting the reactor are size selected and analyzed with a variety of on- and off-line methods. The complete setup, summarized in Figure 1, allows a three-dimensional dataset of particle size vs. composition vs. reaction time to be acquired. Online elemental analysis is performed with the Nano Aerosol Mass Spectrometer (NAMS) [Klems and Johnston, 2013] Online molecular analysis is performed with Extractive Electrospray Ionization (EESI) [Horan et al., 2012] and/or Droplet Assisted Inlet Ionization (DAII) [Horan et al., 2017]. Offline molecular analysis is performed by collecting particles with a spot sampler (SS) followed by High Resolution Mass Spectrometry (HRMS) [Tu and Johnston, 2016].

Figure 1: Schematic of the experimental setup. Reactants A and B mix in the flow tube. The location of the injector in the tube determines the reaction time. Particle size selection is performed with a DMA followed by multiple offline and online analysis methods.
Modeling of particle growth and composition is performed with an iterative algorithm that includes condensation, partitioning and particle phase reaction pathways. The algorithm takes into account the particle size dependence of the mass flux of gas phase species to the particle surface and the radius-of-curvature (Kelvin) effect on molecular volatility.

RESULTS AND CONCLUSIONS

The impact of accretion chemistry on particle growth and composition is illustrated in Figures 2 and 3 for two different types of secondary aerosol. Accretion reactions produce nonvolatile oligomer products that may contain several tens of carbon atoms per molecule, and these reaction products can constitute up to 50% of the total biogenic secondary organic aerosol (SOA) mass in laboratory experiments [Hall and Johnston, 2011]. Figure 2 shows results for SOA produced by β-pinene ozonolysis. In this experiment, size-selective particle analysis is performed for SOA produced at a specific time point in the reaction. The oligomer content relative to the total organic content is found to increase approximately linearly with increasing particle size. A linear increase is expected for a volume-limited process such as accretion chemistry relative to a surface-limited process such as condensation.

Figure 2 (left): Percentage of the total ion signal intensity (SI) due to oligomers having >18 carbon atoms per molecule vs. particle diameter for SOA produced from β-pinene ozonolysis. Figure 3 (right): Ratio of dimer to ring-opened product ion signal intensity (SI) vs. aerosol volume-to-surface area ratio for secondary aerosol produced by OH oxidation of D₅₃.

Figure 3 shows results for secondary aerosol produced from OH oxidation of decamethylcyclopentasiloxane (D₅₃), where the composition of polydisperse aerosol is investigated as a function of aerosol mass loading and hence volume to surface area ratio. Nonvolatile molecular products include two main sources: 1) ring-opened molecules that are produced directly in the gas phase with low enough vapour pressures that they undergo condensation, and 2) dimer molecules composed of two covalently-bound D₅₃ rings that are produced by accretion chemistry in the particle phase. The ratio of dimers to ring-opened products (Figure 3) is found to increase approximately linearly with increasing volume-to-surface area ratio as expected for volume- vs. surface-limited processes. Note that since the volume to surface area ratio for a particle is 2d/3 where d is the particle diameter, the volume to surface area ratios over which accretion chemistry becomes important for the two systems in Figures 2 and 3 are similar.

Figures 4 and 5 show the results of a simplified kinetic model that includes condensation of a gas phase species (NVOC-g, C* = 10⁴ µg/m³), partitioning of a semivolatile species (SVOC, C* = 1 µg/m³), and an accretion reaction in the particle phase where two SVOC molecules react to give a nonvolatile dimer product (NVOC-p, kₙ = 10⁻² M⁻¹s⁻¹). When only condensation and partitioning are included in the model, the growth rate and chemical composition become independent of particle size above about 20 nm in diameter (Figure 4, C+P plot). When the accretion reaction is included, the particle growth rate (C+P+R
in Figure 4) and the accretion product mass fraction (NVOC-p in Figure 5) both increase linearly with increasing particle size, as would be expected for a volume-limited process.

Figure 4 (left): Growth rate vs. particle diameter for a) condensation and partitioning (C+P), and b) condensation, partitioning and accretion reaction (C+P+R). Figure 5 (right): Mass fractions of condensation product (NVOC-g), partitioned semivolatile product (SVOC) and accretion product (NVOC-p) at three different particle diameters for the simulation that includes accretion reaction.

Together, the experimental and modeling studies in Figures 2-5 illustrate the potential impact that particle phase chemistry can have on nanoparticle growth and composition, and the particle size range (tens of nanometers) where this chemistry becomes important.

ACKNOWLEDGEMENT

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REFERENCES


SESSION 7:
Nucleation, Fundamentals

Paul Winkler: Three-phase contact line properties of critical clusters
determined from heterogeneous nucleation experiments

Donguk Suh: Seed shape effect of heterogeneous droplet, bubble, and crystal
nucleation by molecular dynamics

Vitaly Shneidman: Statistics of nucleation in small and large systems

Reinhard Strey: Experimental confirmation of the Knudsen effect in
nanoporous insulation materials

Tereza Trávníčková: Novel approach in binary nucleation experiments
performed under laboratory conditions

Michael Anisimov: New vapor embryos nucleation rate on a droplet surface
in a dry gas flow
THREE-PHASE CONTACT LINE PROPERTIES OF CRITICAL CLUSTERS DETERMINED FROM HETEROGENEOUS NUCLEATION EXPERIMENTS

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Keywords: HETEROGENEOUS NUCLEATION, CONTACT ANGLE, LINE TENSION, NUCLEATION THEOREM.

INTRODUCTION

Formation of aerosols and clouds is related to vapor-to-liquid nucleation processes. In heterogeneous nucleation critical molecular clusters appear on particle surfaces. The interaction of a solid substrate with a (partially) wetting liquid and a gas is oftentimes characterized by the macroscopic Young contact angle between solid and liquid surfaces in the vicinity of the three-phase contact line.

A schematic of a newly formed cluster on a seed particle with radius \( r_p \) can be seen in Figure 1. Applying a macroscopic liquid drop concept, Fletcher (1958) has used a contact angle to approximately describe the interaction between clusters and the underlying particle surface. The Fletcher theory has been applied to a number of different compounds. Experiments on heterogeneous nucleation of water vapor on Ag nanoparticles resulted in large discrepancies from the Fletcher theory, if the macroscopically measured Young angle is used in the calculations (Kulmala et al., 2001). Notably, these deviations can be strongly reduced by choosing a smaller value for the contact angle (Wagner et al., 2003). This observation indicates that a microscopic contact angle relevant for heterogeneous nucleation can be significantly different from the macroscopic Young angle. While contact angles in the macroscopic scale have been measured for various compounds little information is available about microscopic contact angles. Gibbs (1878) already pointed out that an additional force term due to the increased curvature of a strongly curved contact line may distort the macroscopic contact angle. The nanoscale force balance accounting for line tension yields the microscopic contact angle \( \Theta \) expressed by the generalized Young equation (e.g., Pompe and Herminghaus, 2000)

\[
\cos \Theta = \cos \Theta_y - \frac{\kappa_g}{\sigma_L},
\]

where \( \Theta_y \) is the macroscopic Young angle, \( \sigma_L \) surface tension \([\text{J/m}^2]\), and \( \kappa_g \) line tension \([\text{J/m}]\). Here, \( \kappa_g \) refers to geodesic curvature of the contact line which is the curvature of this line viewed as a curve on the substrate surface. For a decreasing line tension term the microscopic contact angle approaches the macroscopic one. Only for sufficiently strong contact line curvature will wetting be influenced by the action of line tension. Here we show that microscopic contact angle \( \Theta \) and angle \( \Phi \) (see Fig. 1) can be determined directly form heterogeneous nucleation experimental data allowing for quantitative determination of line tension \( \kappa_g \) (Winkler et al., 2016).

METHODS

To obtain quantitative experimental information on microscopic contact angles more detailed knowledge about the critical clusters formed at the particle surface during heterogeneous nucleation is required. The
(excess) number $n^*$ of molecules in a heterogeneously formed critical embryo can be directly determined from the heterogeneous nucleation theorem (Vehkamäki et al., 2007)

$$n^* + 1 = \frac{\partial \ln \left( \frac{1}{1 - P} \right)}{\partial \ln S},$$

(2)

where $P$ is heterogeneous nucleation probability and $S$ saturation ratio. Under the assumption of incompressibility of the condensing liquid the volume of a critical cluster can be directly determined as $v^* = n^* v_l$, where $n^*$ is obtained from eq. (2) and $v_l$ is the molecular volume of the bulk liquid. Furthermore, the radius of curvature $r^*$ of a critical cluster is given by the Kelvin relation (Thomson, 1871)

$$r^* = \frac{2 v_l \sigma_{lv}}{kT \ln S},$$

(3)

describing equilibrium vapor pressure conditions over curved surfaces. Here $S$ represents the saturation ratio of the condensing vapor, $T$ is the system temperature and $k$ Boltzmann's constant. The Kelvin relation has been evaluated by experiments on homogeneous (e.g., Strey et al., 1994) as well as heterogeneous (Winkler et al., 2012) nucleation and its predictions have been found to agree within experimental error for various compounds and cluster radii down to a scale of 1 nm.

![Figure 1. 2D-schematic illustrating the geometry of a cluster when formed on a seed particle with radius $r_p$. The newly formed cluster is characterized by the radius of curvature $r^*$ from the Kelvin relation and the number of molecules $n^*$ from the heterogeneous nucleation theorem. Interaction between cluster and particle surface leads to corresponding contact angle $\Theta$ and angle $\Phi$. Based on the above critical cluster properties the (microscopic) contact angle $\Theta$, angle $\Phi$, and hence geodesic curvature $\kappa_g$ of the contact line can be directly determined. We consider heterogeneous nucleation of a supersaturated vapor on nearly spherical particles with radius $r_p$ at the onset saturation ratio $S_{\text{onset}}$, at which 50% of the particles are activated during a certain nucleation time period. From the nucleation theorem (2) we can determine the number $n^*$ of molecules in the critical embryo and hence the critical embryo volume $v^*$. From the Kelvin relation (3) we obtain the radius of curvature $r^*$ of the critical embryo corresponding to the saturation ratio $S_{\text{onset}}$. As can be seen from the cluster geometry shown in Fig. 1, knowledge of $r_p$, $r^*$ and $v^* = n^* v_l$ is sufficient for a unique determination of the contact angle $\Theta$ and angle $\Phi$.

We have determined microscopic contact angles $\Theta$ and angles $\Phi$ from experimental data on heterogeneous nucleation of water vapor on Ag particles (Kupc et al., 2013). The experimental procedure has been described in detail elsewhere (Wagner et al., 2003). Measurements were done at a nucleation temperature of 278 K using mobility diameters of 3.5, 5.5 and 7.0 nm. The corresponding geometric
particle diameters relevant for the present study are smaller than the mobility diameters by 0.3 nm (Larriba et al., 2011). The shape of the particles was analyzed in a transmission electron microscope and an approximately spherical shape of the Ag particles was observed. Using the results of the evaluation critical cluster geometry is shown to scale in Fig. 2. We find that the microscopic contact angles obtained are considerably smaller than the corresponding macroscopically measured equilibrium Young angle $\Theta_Y$ of approximately 90° (Wagner et al., 2003). Remarkably, we now have all quantities available to determine line tension. Based on equation (1) line tension $\tau$ is found to be $-(0.92 \pm 0.1) \times 10^{-10} \text{J/m}$ on average, accounting for experimental uncertainties resulting from the heterogeneous nucleation experiments.

![Figure 2. Cluster geometry shown to scale for different seed radii and corresponding H$_2$O cap radii of curvature. Distances in nm.](image)

Interestingly, we find negative values for line tension which also have been predicted by Gibbs (1878). In fact, a recent modelling study of Lennard-Jones nanodrops reports that negative values of line tension lead to reduced microscopic contact angles and that line tension is the dominant mechanism for the size dependence of the contact angle (Weijs et al., 2011). It is also worth noting that the ratio $\sigma_v/\tau$ (see eq. 1) provides a characteristic measure of contact line curvature and is found to be on the order of $-1 \text{nm}^{-1}$. This is the scale where line tension effects on contact angle come into play. A negative line tension indicates strong seed-cap interaction at this scale that favors wetting of the seed and leads to smaller contact angles, as obtained in the present study from experimental nucleation data.

While we find negative values of line tension for the system water-silver, line tension may also have positive values for different systems and is sensitive to temperature (Wang et al, 1999; Wi et al., 2011). It is worth noting though that the absolute value of $\tau$ found in our study agrees nicely with recent experimental studies based on atomic force microscopy (McBride and Law, 2012) and fits well to theoretical predictions (Bresme and Oettel, 2007).

CONCLUSIONS

Our study clearly shows that three-phase contact line properties such as contact line curvature, microscopic contact angle and line tension can be directly determined on a scale of 1 nm (Winkler et al., 2016). The evaluation based on heterogeneous nucleation experiments is not reliant on nucleation theory and only requires incompressibility of the condensing liquid. Besides several other applications microscopic contact angles are important for consistent use in heterogeneous nucleation theory. So far the contact angle has often been considered as a free parameter in heterogeneous nucleation theory. In some experiments the macroscopically measured Young angle was used (Kulmala et al., 2001), in other studies the contact angle was varied in order to fit Fletcher theory to experimental data (Wagner et al., 2003). Generally, these approaches result in inconsistencies or even large discrepancies from corresponding experimental data (Kulmala et al., 2001). Use of the microscopic contact angle and the line tension as
derived in this study enables an improved geometrically consistent theoretical description of heterogeneous nucleation on (partially) wettable particles.

It should be noted that contact angles and line tensions derived above were obtained for spherical geometry. On the molecular scale deviations from an ideal spherical shape are likely to occur. In this case the effective contact angle and line tension obtained can be viewed as a surrogate for surface interaction. The fact that the microscopic contact angles differ from the Young (macroscopic) contact angle is likely due to microscopic interactions that occur on the molecular scale and can be attributed to line tension. Line tension should therefore be carefully considered during the initial steps of phase transition on nanosized objects such as in nanoparticle and cloud formation.

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REFERENCES


INTRODUCTION

Phase transitions originate from heterogeneous nucleation, which is a ubiquitous phenomenon seen in nature and is applied to various fields in the industry. (Fernando, Shortell, Vernon, Jaatinen, & Waclawik, 2015; Knight, Devrues, & Oolman, 1984). The phenomenon is the source of different products such as vapor condensing into droplets, cavitation, and crystallization. Depending on the supersaturation ratio, nucleation can occur stochastically in the nanoscale, and therefore it is very difficult to observe directly in experiments. With the constant developments in computers, however, molecular simulations, and namely, molecular dynamics has become a powerful tool in studying nucleation (Carvalho & Dalnoki-Veress, 2010; Matsumoto, Saito, & Ohmine, 2002). Some of the first studies on homogeneous or heterogeneous nucleation using molecular dynamics were for homogeneous vapor systems or vapor nucleating on solid surfaces (Maruyama & Kimura, 2000; Yasuoka & Matsumoto, 1998). Heterogeneous nucleation, however, more commonly occurs from a three-dimensional impurity freely moving in its original phase. One of the first studies of heterogeneous nucleation on basic geometries was conducted by Inci and Bowles, where they studied how condensation will occur on a spherical seed particle in a supersaturated vapor (Inci & Bowles, 2011). Heterogeneous bubble nucleation on a solid surface has been studied by Novak et al. (Novak, Maginn, & McCready, 2007). Suh et al. analyzed how bubble formation will be affected by an addition of a seed particle (Suh, Nakamura, & Yasuoka, 2015). Jungblut and Dellago have simulated crystallization on prestructured seed particles with different unit lattice structures (Jungblut & Dellago, 2013). Though there have been numerous studies on more specific substances such as sulfuric acid and organic molecules (Darvas, Picaud, & Pal, 2011; Matsubara, Ebisuzaki, & Yasuoka, 2009), more focus is necessary on fundamental geometries to understand the actual physics of the phenomenon.

Heterogeneous nucleation for droplet condensation and bubble formation has been conducted for insoluble seeds with different configurations by Suh et al. (Suh & Yasuoka, 2011, 2012, 2013, 2016; Suh, Yasuoka, & Zeng, 2015). This study reviews the source of the shape effect and how the interface of the seed surface affects the rates of the aforementioned phase transition processes including crystallization. The next section will summarize the simulation setup and the results will follow.

METHODS

A constant particle number, volume, temperature ensemble was employed by controlling the temperature with velocity rescaling (Sadus, 2002). An example of a system is in Fig. 1(a) for the supersaturated liquid. This system was made by initially placing argon molecules that have Lennard-Jones parameters, and inserting a spherical or cubic seed particle with aluminum Lennard-Jones parameters based on reference [14]. Further details about the setup are in references (Suh, Nakamura, et al., 2015; Suh & Yasuoka, 2011, 2012). Quenching to certain target temperatures after equilibration was performed for all systems to control the supersaturation.

All interactions were done by the Lennard-Jones 12-6 potential and the Lorentz-Berthelot relations were used for argon and aluminum atom interactions. A Stillinger radius of 1.5 \( \sigma_{\text{Al}} \) was used to identify a cluster and a void size of 2.6 \( \sigma_{\text{Ar}} \) and a threshold length of 1.4 \( \sigma_{\text{Ar}} \) was used to analyze a bubble and crystal, respectively (Lechner & Dellago, 2008).
RESULTS

Though the surface area of the seeds for size class 108, 256, and 500 are less than 5%, a simple change in the geometry of the seed from sphere to cube will increase the condensation (growth) on the seed surface by a factor of 3–10 and this is consistent over a broad range of supersaturation ratios as shown in Fig. 2(a). On the other hand, the formation time for bubbles does not show a clear shape effect. The biggest difference between droplet and bubble nucleation reside on whether the molecules in the original phase recognize the surface curvature of the seed. Vapor molecules will certainly realize the curved surface of a seed particle so the effect is evident in condensation. On the other hand, as seen in Fig. 1(b) a bubble does not form on the seed surface, so the curvature of the seed becomes insignificant (Suh, Nakamura, et al., 2015).

Figure 1. Sliced snapshots for (a) onset of bubble formation and (b) simultaneous crystallization and bubble formation for a cube at extreme quenching to 50.2K.

Figure 2. Growth rate comparisons for cube and sphere for (a) condensation [Reprinted with permission from Journal of Physical Chemistry B 2012, 116 (50), pp 14637–14649. Copyright 2012 American Chemical Society.] (b) bubble nucleation.
Crystal formation starts similarly to bubbles but from a denser liquid. Figure 3 shows that the formation time difference for the cube and the sphere increases as the supersaturation decreases, which is evidence of the existence of a shape effect. Unlike bubble formation, crystals will start growing on the seed surface by epitaxy so the surface that does not have curvature is favorable.

CONCLUSIONS

Heterogeneous nucleation of droplets, bubbles, and crystals for systems with an insoluble particle immersed inside a supersaturated system was simulated by molecular dynamics. The source of the shape effect was found to be from the curvature of the seed. The liquid condensation and crystal formation were clearly influenced by the seed shape, whereas the effect of bubble formation was insignificant. Further efforts will be made to be able to present more quantitative results in the future.

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REFERENCES


STATISTICS OF NUCLEATION IN SMALL AND LARGE SYSTEMS

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Keywords: Dynamic Monte Carlo, Lattice Gas, Cavitation.

INTRODUCTION

Small nucleating systems are encountered naturally (e.g., ice nucleation in small droplets, biological nucleation), can be produced artificially (e.g., in solidification studies) or appear in Monte Carlo and Molecular Dynamics simulations. In such systems, typically only a single nucleus is formed and the waiting time to detect this nucleus fluctuates enormously. Alternatively, in large systems one observes a finite (moderately large) number of growing nuclei \( \rho(t) \). Statistical fluctuations are present, but are less prominent in such systems, and adequate identification with the small scale data can be important for a proper understanding of the nucleation mechanism.

Traditional early methods of analysis used \( \bar{t} \), the average waiting time to observe the first nucleus, as a way to evaluate the homogeneous nucleation rate \( I \sim 1/N \bar{t} \), where \( N \) is the number of monomers in the system. This, however, is justified for extremely rare nucleation events, when \( 1/N I \) exceeds all other time scales, and when \( \bar{t} \) is independent of the size \( n \) of the nucleus being detected. Other interpretations of \( \bar{t} \), with broad applications were developed recently - see e.g. (Reguera, 2013) and references therein, but the general problem of extracting reliable nucleation information from statistical data still requires clarification.

The intent of this presentation is to use the earlier matched asymptotic ("singular perturbation") solution of the time-dependent Becker-Döring equation (BDE) in order to formulate a method of analysis which can be applied to both small and large systems. In particular, the role \( \sigma \), the standard deviation of the distribution of waiting times, is emphasized as an accurate way to evaluate the inverse stationary rate \( 1/N I \) even in situations when time-dependent effects are non-negligible.

The method is applied to two problems which are beyond the simple Becker-Döring model, but which nevertheless allow a rigorous analysis. The first is condensation of a supersaturated lattice gas (LG) driven by Metropolis dynamics - see (Binder and Virnau, 2016) for an overview of high-temperature results. In addition, at low temperatures computer assisted analytical evaluations of the rate can be obtained from cluster expansions (Shneidman and Nita, 2006). This makes the LG a unique non-classical nucleation system for which accurate formulas for both steady and transient rates can be derived from "first principles". The results of large scale Monte Carlo simulations can be processed using the suggested statistical approach, and can be compared with analytics, which thus provides a strict independent test.

The second group of problems are related to cavitation in a stretched fluid (Brennen, 1995). Cavitation can be described as a random walk of nucleus in the multidimensional space of its parameters, similarly to binary nucleation. However, due to inertia of the surrounding fluid, direct methods of solution of the associated Fokker-Planck equation have to be replaced by stochastic modeling. In those cases the proposed statistical analysis becomes useful and allows to establish the limits of applicability of available analytical results.
METHODS

The probability density function (PDF) \( w(t) \) for the distribution of waiting times and the cumulative distribution (CDF) \( F(t) \) can be related to nucleation parameters as

\[
w(t) = j(n, t) e^{-\rho(t)}
\]

\[
F(t) = 1 - e^{-\rho(t)}
\]

Here \( n \) is the "size" of the observed nucleus (assumed larger than the critical size \( n_* \)), \( j(n, t) \) is the nucleation flux with a stationary limit \( N I \) and \( \rho(t) = \int_0^t dt' j(n, t') \) with a large-time asymptote \( NI (t - t_0) \) where \( t_0(n) \) is the "time lag".

In case nucleation is described by the BDE, the time scales can be obtained from the associated deterministic growth rate \( \dot{n}(n) \) which changes sign at \( n = n_* \). The smaller scale \( \tau \) is defined as the inverse of \( d\dot{n}/dn \) at \( n = n_* \) and enters into the preexponential of the stationary Zeldovich formula for \( I \). An additional, larger time scale \( t_i(n) \) ("incubation time") appears in the transient solution (Shneidman, 1987, 1988). This time scale logarithmically depends on the dimensionless nucleation barrier \( B \), containing a term \( \tau \ln B \) and is related to the aforementioned time lag by \( t_i = t_0 - 0.5772\tau \); otherwise it also depends on size \( n \) and is sensitive to a specific growth rate \( \dot{n}(n) \) - see (Shneidman, 1988). In the present study of interest is only the robust part of the solution, which is independent of the specific form of the BDE and which is given by

\[
j(n, t) = NI \exp \left[ -e^{-r} \right] , \quad r = \frac{t - t_i(n)}{\tau}
\]

\[
\rho(t) = NI\tau E_1(e^{-r})
\]

Here \( E_1 \) is the first exponential integral (Abramowitz and Stegun, 1972), and in a large system with \( NI\tau \gg 1 \) the function \( \rho(t) \) describes the number of nuclei exceeding size \( n \).

For a small system with \( \epsilon = NI\tau \ll 1 \) the characteristic time is large, and one can further simplify the PDF by using the asymptote of the exponential integral and adjusting the constant to preserve normalization. In terms of dimensionless reduced "time" \( r \) defined in eq.(3)

\[
w(r) \simeq \epsilon \exp \left[ -e^{-r} - \epsilon r \right] /\Gamma(1 + \epsilon)
\]

Evaluating the moments of the distribution one has

\[
\bar{t}(n) \simeq \frac{1}{NI} + t_0(n) - \frac{1}{6NI} (\pi\epsilon)^2
\]

\[
\sigma \simeq \frac{1}{NI} + \frac{1}{12NI} (\pi\epsilon)^2
\]

Even without the assumption \( \epsilon \ll 1 \), the standard deviation \( \sigma \) is independent of the cluster size \( n \), in clear contrast with \( \bar{t}(n) \) which grows as \( \int dn/\dot{u} \).

Nucleation in 2D Lattice Gas (LG)

A supersaturated LG is equivalent to the Ising model with nearest-neighbor interaction placed in external magnetic field, with spins originally pointing in the "wrong" direction. Metropolis-type dynamics of spin flips is added to allow transition to the stable phase. This transition proceeds
via nucleation and growth of islands, and in Monte Carlo (MC) simulations looks remarkably realistic. While such simulations, as well as the LG model itself, are often considered less true to life than, say molecular dynamics, they nevertheless exhibit unique features both in computational and analytical aspects. For example, due to discrete lattice structure computations are much faster and allow to explore much broader domain of temperatures $T$ and supersaturations $S$. Identification of a "cluster" is straightforward. In equilibrium the 2D Onsager solution provides the exact surface tension, allowing to specify predictions of the classical theory at all $T$ and small $S$. Alternatively, at small $T$ and finite $S$ only a limited number of cluster configurations contribute to nucleation. This allows analytical (generally, computer assisted) evaluation of the stationary rate $I$ and efficient semi-analytical description of transient nucleation in LG (Shneidman and Nita, 2006). Comparison with MC results then can be made, bypassing the classical theory except for using statistics suggested by the solution of the Becker-Döring equation.

The above is illustrated in Fig. 1. The standard deviation -open symbols in the right panel- indeed does not depend on the size $n$ of a cluster and accurately corresponds to independent semi-analytical data for the inverse rate. Data for a large system with $N \sim 10^6$ (not shown) lead to similar results.

![Figure 1](image.png)

**Figure 1:** From (Shneidman, 2014). Left: The probability distribution function (PDF) for the waiting times for the first nucleus in a lattice gas on a square lattice with $N \simeq 20000$. Symbols - Monte Carlo (MC) data (binned). Lines: solid - from eqs. (1, 3, 4), smooth dashed - elementary approximation, eq. (5), sharp dashed - delayed exponential. Right: MC data for the mean of waiting times (solid symbols) and their standard deviation (open symbols) as functions of the "size" $n$ (number of spins) in a detectable cluster. The horizontal straight line is $1/N I$ with $I$ found from low-temperature cluster expansions (Shneidman and Nita, 2006). No matching parameters were used.

### Cavitation

The complexity of the cavitation problem, even in its simplest near-classical formulation, comes from the fact that generally a bubble is characterized by several random variables (size, growth/decay rate, pressure, etc.), leading to multiparametric nucleation. New issue are added, for example the selection of an adequate diffusion tensor $\hat{D}$ in the associated Fokker-Planck equation (which will be discussed in the presentation) or the actual solution of such an equation. In particular, in the presence of inertial effects $\hat{D}$ becomes non-symmetric and direct methods of solving the Fokker-Planck equation can become unstable. Subtle analytical issues (which mirror those in the celebrated Kramers problem) also arise. In addition, post nucleation growth of a bubble is described by a non-linear Rayleigh-Plesset equation (Brennen, 1995) which does not allow for an exact solution, further complicating description of the phase transformation (Shneidman, 2016).

To describe cavitation in a viscous inertial fluid a Langevin equation for random evolution of
a bubble in a fluctuating pressure field was simulated for moderate inertial effects \( (r_{\text{in}} \simeq 5 \) in notations of the indicated reference). The aforementioned statistical analysis was used to process the resulting data. A typical example based on evolution of a single bubble (i.e., \( N = 1 \)) is shown in Fig. 2. Even for a modest barrier \( B \simeq 8 \) very large sizes had to be considered in order to distinguish between \( \bar{t}(R) \) and \( \sigma \simeq \text{const} \).

Figure 2: Cavitation data from the Langevin equation for a single bubble. The mean of waiting times \( \bar{t} \) (solid symbols) and their standard deviation \( \sigma \) (open symbols) are shown for different sizes \( R \) of a detectable bubble; times are multiplied by \( I \) where \( I \approx 0.00193 \) in units considered, based on classical theory. The horizontal straight line is the average of \( \sigma \) for \( R \geq 100R_* \). Dashed line corresponds to \( \bar{t} \approx 1/I + t_0(R) \) with \( t_0 \) from eq. (33) in (Shneidman, 2016).

REFERENCES


EXPERIMENTAL CONFIRMATION OF THE KNUDSEN EFFECT IN NANOPOROUS INSULATION MATERIALS

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Keywords: nanoporous polymer, PMMA, Knudsen effect, thermal insulation, nanoporous insulating material.

INTRODUCTION

Nanoporous insulating materials (NIMs) promise enormous energy savings through improved thermal insulation properties (Jelle et al. 2010). Unfortunately, no cost-efficient generation of such materials on the large scale is in sight due to the necessity to apply high pressures of blowing agent or supercritical drying. Grassberger et al. (2017) have developed an ambient pressure method for preparation of nanoporous materials, which utilizes PMMA (polymethylmethacrylate) beads swollen in a mixture of two miscible solvents (e.g. acetone and cyclohexane), one of which (acetone) is a swelling agent for the polymer. When drying the swollen beads, sequential evaporation of the two liquids (acetone evaporates more readily than cyclohexane) leaves behind nanoporous polymer beads. The internal structure as visualized by SEM (c.f. Figure 1) shows a spongy morphology (Grassberger 2016).

![Nanoporous PMMA](image)

Figure 1. Nanoporous PMMA. By simple suspension polymerization with various amounts of crosslinker PMMA beads of millimeter size were generated. After swelling the beads and sequential evaporation of the solvents nanoporous PMMA material with pore sizes varying between 80 and 800 nm was obtained. Note the spongy, open-celled nanostructure with a porosity of about \( P \approx 0.7 \). For details refer to Grassberger et al. (2017).

For various average pore sizes we measured the gas thermal conductivity and found enormous reductions as pressure or pore size decrease. Interestingly the individual gas thermal conductivities scale and collapse onto a single curve as quantitatively predicted by the Knudsen effect. (c.f. Figure 2).
THEORY

The thermal conductivity $\lambda$ of an insulating nanoporous material consists of three contributions, the heat transfer by (infrared) radiation $\lambda_{\text{radiation}}$, the heat conduction through the solid matrix $\lambda_{\text{solid}}$, and heat conduction by the cell gas $\lambda_{\text{gas}}$. 

$$\lambda = \lambda_{\text{radiation}} + f(1 - P)\lambda_{\text{solid}} + P\lambda_{\text{gas}}$$

where $P$ is the porosity and $f < 1$ is a tortuosity factor taking into account the irregular nature of the matrix (Lu et al. 1995, Notario et al. 2015). For ordinary insulation foams the heat conduction by the cell gas accounts for more than two thirds of the thermal conductivity (Placido et al. 2005). Thus, taking advantage of the Knudsen effect the gaseous thermal conductivity can be lowered enormously, if the pore size is made comparable to or smaller than the mean free path length $l_{\text{mean}}$ of the enclosed gas molecules. $D_{\text{pore}}$ is the pore diameter of the porous material. Knudsen in 1909 introduced the ratio of the two numbers (hence the name Knudsen number)

$$Kn = \frac{l_{\text{mean}}}{D_{\text{pore}}}$$

where $l_{\text{mean}}$ of the gas molecules is given by

$$l_{\text{mean}} = \frac{k_B T}{\sqrt{2\pi d_m^2} p}$$

with $d_m$ the molecular diameter ($d_m = 0.36$ nm for air (Kennard 1938), $p$ the pressure, $T$ the temperature and $k_B$ the Boltzmann constant. The Knudsen effect is characterized by (Lu et al. 1995, Jelle et al. 2010)

$$\lambda_{\text{gas}} = \frac{\lambda_{\text{gas,0}}}{1 + 2\beta Kn}$$

where $\lambda_{\text{gas,0}} = 0.0262$ mWm$^{-1}$K$^{-1}$ is the thermal conductivity of air (Lemmon and Jacobsen 2004), $\beta$ a parameter that takes the energy transfer between the gas molecules and the limiting solid structure into account ($\beta = 1.5$ for air (Jelle et al. 2010)). Obviously, increasing the mean free path length of the gas by reducing the pressure or decreasing the pore size increases the Knudsen number and in consequence $\lambda_{\text{gas}}$ decreases.

EXPERIMENT

In Figure 2, left, the gas thermal conductivities are measured as function of pressure. Note that with decreasing pore size the gas thermal conductivity vanishes.

![Figure 2](image-url)

Figure 2. Left: Measured gas thermal conductivities as function of pressure for porous materials. Right: Scaling of gas thermal conductivities vs. Knudsen number; full line calculated according to theory, eq. 3 with $\beta = 1.5$. 
We note that by plotting in Figure 2, right, the data versus the Knudsen number all data fall strikingly (within experimental uncertainty) onto a single curve calculated from equation 3.

DISCUSSION

We noted earlier that the Knudsen effect in gas phase growth of water droplets provided an amazingly accurate description of the transition regime (Fladerer et al. 2002, Miles et al. 2010, Seinfeld and Pandis 1998). Here we found further striking evidence of the validity of the Knudsen concept. A number of interesting observations can be discussed. 1) The well-known theoretical independence of the gas thermal conductivity on pressure is borne out by the measurements on the two macrofoams (Styropor® with 200μ and Armaflex® with 300μ cellsizes, respectively). 2) The thermal conductivity decreases as the total pressure is decreased as soon as the pore size drops below 1 micron. Therefore, if low pressure is an option, as in vacuum isolation panels (VIPs), or is given, as in space applications, like for satellites in the orbits around the earth, a mean pore size of 1 micron may suffice. This aspect is of interest for production of nanoporous materials, as it is easier to reach low densities of the polymer matrix, if the requirement of extremely small pore size is relaxed. 3) The scaled plot in Figure 2, right, shows that the Knudsen number apparently is the only relevant tuning parameter, not the pressure or the pore size alone. Thus we provide experimental gas thermal conductivities over more than six orders of magnitude of the corresponding Knudsen numbers in conjunction with a perfect description by eq. 3 without any adjustable parameter (β=1.5 has been suggested by previous workers based on theoretical arguments). 4) As has been mentioned previously (Grassberger et al. 2017) our results confirm and supplement Notario et al.’s (2015) results on different nanoporous materials quantitatively. 5) Before application as low-cost insulation materials the porosities of our nanoporous polymeric materials have to be increased (or the densities reduced). This task in mind several thesis works (Müller 2013, Oberhofer 2015 and Grassberger 2016)) were devoted to investigate the density - pore size trade off. To date the lowest pore sizes have the highest densities and vice versa. Here the efforts are continuing. 6) Here we have demonstrated substantial progress in reducing the gas thermal conductivity. For application, however, also contributions by radiation and solid conduction to λ will need to be considered (Placido et al. 2005, Notario et al. 2015)

CONCLUSIONS

The Knudsen effect on transport properties is well-known to atmospheric scientists and gas phase workers when particle dimensions become comparable to the mean free path of the gas molecules (Seinfeld and Pandis, 1998). In this work we explore the beneficial effect on the gas thermal conductivity that occurs in nanoporous insulation materials (Jelle et al. 2010). The required high pressure of blowing agents or supercritical extraction procedures is a major obstacle in industrial production processes of nanoporous materials. Grassberger et al. (2017) demonstrated a new method for generating nanoporous polymer materials without gaseous blowing agent at ambient conditions. By swelling crosslinked PMMA beads in specially selected solvents leads to nanostructured PMMA materials with mean pore diameters as low as $D_{pore} = 80$ nm (c.f. Figure 1). Varying the crosslink density nanoporous PMMA materials with different pore sizes were generated. For these materials the gas thermal conductivity was measured as function of pressure. In addition the gaseous thermal conductivity of conventional microfoams (Styropor® with 200μ and Armaflex® with 300μ cellsizes, respectively) was measured for comparison (c.f. Figure 2, left). The effect of the mean free path limitations in the nanoporous materials (the Knudsen effect) becomes obvious considering Figure 2. By decreasing the pore size, the sigmoidal evolution of the gaseous contribution to the thermal conductivity shifts to higher pressure. Remarkably, all measured data points collapse onto a single curve that is quantitatively predicted by the Knudsen effect (c.f. Figure 2 right). Our best nanoporous PMMA material has a three times better gaseous thermal insulation at ambient conditions than c.g. Styropor® or Armaflex®.
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REFERENCES

Kennard EH (1938) _Kinetic theory of gases with an introduction to statistical mechanics_. Mc Grow Hill, New York
NOVEL APPROACH IN BINARY NUCLEATION EXPERIMENTS PERFORMED UNDER LABORATORY CONDITIONS

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Keywords: BINARY NUCLEATION, SULFURIC ACID – WATER, LAMINAR CO-FLOW TUBE.

INTRODUCTION

Binary and ternary nucleation of secondary aerosols form the significant part of atmospheric nucleations. Current inability to describe the process of atmospheric nucleation correctly causes uncertainties in the prediction of climatic changes whether in local or global scale. To overcome this problem, several experimental devices have been developed to study both, homogeneous or heterogeneous nucleation of aerosols in the laboratory (see for example (Wyslouzil and Wölk 2016) and references therein). Using of different experimental devices, however, leads to differences in results, inexplicable at the current level of knowledge. For this reason, it is essential to obtain more experimental data based on various experimental techniques. Mutual comparison of obtained results can contribute to understanding the nature of nucleation processes, as well as to revealing or overcoming weaknesses of used methods.

METHODS

Experimental device

In this work we introduce a novel device especially designed for binary or ternary nucleation experiments – a laminar co-flow tube (LCFT). The first experiments performed on this type of device were focused on binary nucleation of sulfuric acid-water. Main advantage of the co-flow design of LCFT is, that the turbulent mixing zone is not present. Simple modeling of laminar flow then leads to more accurate determination of location and composition of nucleation zone. The sheath flow of water vapor surrounding the axial sulfuric acid stream prevents the losses of H2SO4 on the chamber wall. A detailed description of the whole experimental device and validation of operational set-up parameters can be found here (Krejčí 2010). At this device, concentrations of newly formed nuclei versus time are measured as an input parameter for mathematical model.

Model for the description of LCFT

Similarly, as in the case of previous studies, the processing of measured particle concentrations leads to the evaluation of the nucleation isotherm - curve of experimental nucleation rate depending on the concentration of sulfuric acid in the nucleation zone for a selected relative humidity of 33% (see Figure 1) and temperature 25°C. To obtain concentration profiles of sulfuric acid and location of nucleation maximum the model solves coupled mass and momentum transport in the three-component system (H2SO4(g), H2O(g), N2(g)). 2D axisymmetric system, steady state incompressible fluid and ideal vapor-gas
mixture is assumed. The effects on the mass transport connected with presence of hydrates of the H$_2$SO$_4$ molecules in the mixture are accounted for into the effective value of the binary diffusion coefficient. Thermal effects associated with mutual interactions between sulfuric acid and water molecules were neglected due to the thermostating effects of exceedance of the carrier gas. The theoretical value of the binary nucleation rate [cm$^3$s$^{-1}$] of sulfuric acid and water vapor mixture was evaluated according to the following function:

$$J_{\text{theor}} = \exp(46.55 + 19.18 \log (Ra) + 3.127 \log (Rh) + 3.127 \log (Ra) \log (Rh))$$

(1) previously published by Wyslouzil et al. (Wyslouzil et al. 1991) as a fit on measured data for the 25°C isotherm.

CONCLUSIONS

The comparison with results published by other authors using various experimental techniques confirmed, that the laminar co-flow tube is able to cover wide range of nucleation rates of the H$_2$SO$_4$-H$_2$O system. The nucleation rates resulting from our LCFT experiment are approximately two orders of magnitude lower than those obtained in chambers with turbulent mixing. Usually, presence of impurities as amines or organic acids cause stabilization of clusters and shifting nucleation isotherms towards higher nucleation rates. The location of our data in the Figure 1 might have been caused either by the use of very pure substances (nitrogen, water, sulfuric acid) and a well-sealed apparatus or by a more accurate mathematical model, derived for the specific construction of the LCFT. Also substantial suppression of loses of the H$_2$SO$_4$ on the walls of the LCFT could lead to higher measured number concentrations of particles and finally also to higher values of experimental nucleation rates. We hope, that our experiments could in the future contribute to the solution of questions about stability of H$_2$SO$_4$-H$_2$O clusters and about effects of impurities present in the atmosphere.

Figure 1. The dependence of the experimental nucleation rate on the concentration of sulfuric acid in the chamber during the constant value of $R_h$ – comparison of our data with results previously published by other authors.

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REFERENCES


NEW VAPOR EMBRYOS NUCLEATION RATE ON A DROPLET SURFACE IN A DRY GAS FLOW

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It was shown by the multiple and systematic researches, that temperature of the droplet surfaces for the various liquids are non-uniform (Terekhov et al., 2010; 2012). The non-uniform surface temperatures result from internal droplet processes that are not dependent on the surrounding gas velocities within some velocity intervals. There does not seem to be scientific literature regarding the mechanisms leading to non-uniform temperature distributions on a droplet surface. Thermographic measurements show that the non-uniform temperature distribution on the droplets surfaces was initiated by spontaneous local centers of the vapor nucleation that can be seen as dots with the decreased temperatures. An experimental system was developed for empirical vapor nucleation studies on evaporating droplets that were fixed within a dry gas flow. The number of evaporating centers and dynamics of their appearance were detected by the infrared imager using a Thermo Tracer TH7102MV. A transition to a steady state regime can be detected on single droplets when the number of observed evaporation centers per the unit time becomes constant. Vapor nucleation rates were measured for the droplets of various single liquids and some water solutions.

The driving force appeared to attain vapor-liquid equilibrium when a droplet is blown by the dry gas. The liquid evaporation rate increases when the evaporated vapor was removed from the vicinity of the droplet. Fluctuations in the temperature appeared on the droplet surface and the local evaporation (or vapor production) can be seen time to time. Evaporation produces local cooling due to the uptake of the latent heat of vaporization from the surrounding liquid. Thermal imaging easily shows areas with reduced temperature on the droplet surface. These areas can be attributed to evaporation from the liquid under investigation.

The droplets with diameters from 1.5 to 2 mm were suspended in dry or unsaturated gas flows. Gas (air) was saturated by water vapor to less than 2% for water droplet studies. Air flow velocities ranged from 1 to 5 m/s and temperature was ~20°C. The basic elements of the experimental system are shown in Fig. 1. The temperature distributions on the evaporating droplet surfaces of water and water solutions were measured using thermography. The temperature measurements accuracy was ≤ 0.2°C.

Digital presentation of the droplet images provides the ability to quantitatively define the droplet size and volume as it moves over time. The integrated evaporation rate from the liquid – vapor interfacial surface as well as the heat-mass transfer coefficients along the interfacial boundary were calculated using the droplet volume variation with time. Details of the data development is presented by Terekhov et al. (2010). Typical droplet shapes are presented in the thermographic images shown in Fig. 2. The droplets surface temperature image was varicolored as a rule indicating that there were variations in temperature across the surface.

The temperature variations appeared spontaneously. Water droplet images with a time step of 5 second are shown in Fig. 2. Considerable temperature irregularity can be observed even for
relatively close points. The droplet surface temperatures at the nearly located crosses are different considerably.

![Diagram](image)

**Fig. 1.** Schematic presentation of the system for a droplet evaporation monitoring
1 – a thermocouple; 2 – suspended droplet of the test liquid; 3 – an infrared imager with a microscope attachment; 4 – a thermocouple signal digitizer and buffer memory; 5 – Computer

![Images](image)

**Fig. 2.** The water droplet images with 5 sec. time interval each other.
The gas-flow temperatures are equal to 20.9°C (upper) and 80.0°C (lower).

The temperature distribution on the droplet surfaces of acetone, methanol, ethanol, and their water solutions were quite similar. The evaporation intensity was characterized by the droplet diameters changing and is presented in Fig. 3. The air flow velocity was approximately 1.5 m/s at a temperature of 23°C. A higher fraction of ethanol in the water droplet led to more intensive droplet evaporation as can be seen in Fig. 3.

The measuring system could not monitor individual evaporation sites, but the number of such events was defined by the decreased temperature areas observed in the thermal images pictures of a droplet. It seems intuitively that all evaporation events are generated in the surface layer of each droplet. The deeper levels of droplet would smooth the geometrical and thermodynamic disturbances in the upper level. The evaluation of radial temperature gradients was not provided at this present stage of this study. The distribution of evaporation centers was assumed to be uniform across the droplet surface. To estimate the nucleation volume, the droplet surface thickness is multiplied by the areas in which the nucleation events are detected by the infrared imaging system.
Fig. 3. The droplet’s diameters (d) variation on time (t) for the water – ethanol solutions.

Fig. 4. The liquid nucleation rates, ω, on time (t) for water-ethanol systems.

The equation \( \omega = N \cdot k(\tau V) \) was used in the nucleation rate calculation, where \( \omega \) is the nucleation rate (i.e., the number of nucleation events per unit volume per unit time). Number of nucleation events was defined for the part of the droplet image (field of vision), which was exposed by an infrared imager with a microscope attachment in the time interval \( \tau = 0.25 \text{ sec} \). \( k \) is shape factor to calculate the total number of the nucleation events along the whole droplet surface. The field of view is less than total droplet surface, thus its value is more than unity. \( \tau \) is the time interval for a single image exposition. \( V \) is the boiling volume, which is equal to the droplet surface times the height of the droplet nucleating cover. We assume that the height is equal to two image pixels approximately. We hope to get more accurate estimation of that height in future work.

Fig. 5. The boiling nucleation rate on the water droplet surface blown by dry air.
Red line is averaged data from two experimental sets.

Results of the droplet diameter and the nucleation rate measurements on the droplet surfaces are presented in Figs. 3 and 4. The results of the changes of diameters and droplet nucleation rate on the droplet surface from time to time are shown in Figs. 3 and 4. Relatively large standard deviation (10%) resulted from the small number of evaporation events and subjective (operator dependent) identification of the low temperature areas. We hope to obtain better statistics and more objective (automatic) counts of nucleation event centers in future experiments.
The average nucleation rates for water droplets with diameters ~2 mm, air velocity near 1.5 m/s and nucleation temperature of 24°C are presented in Fig. 5 for two series of measurements. Standard deviations which was calculated jointly for both series were ~10%. As can be seen in Fig. 5, the nucleation rate increases slightly with time. We think that these data have the qualitatively agreement with Skripov (1980). It is known that the nucleation rate data collected for the same system measured with different systems can have differ by several orders of magnitude. For example, data on the nucleation rates collected using the static and flow diffusion chamber (Bruns et al., 2005) deviated from each other by up to 3-4 orders of magnitude and flow diffusion chamber data deviated from adiabatic expansion two-piston chamber results (Anisimov et al., 1994).

Thus, this new measurement system has provided the opportunity to measure nucleation rates on liquid droplets surfaces in a dry gas flow. The measurement system provides the potential to create a new quantitative measurement method for liquid nucleation rates on droplet surfaces located in a dry gas atmosphere. However, to be able to directly compare the nucleation rate data with this system with those collected using different measuring schemes, we need a consistent set of criteria for the vapor – gas nucleation to obtain data that are independent of the measurement system and then expand that approach to liquid/ solid phase nucleation.

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References:
SESSION 8:
NPF AROUND THE WORLD

Mikko Sipilä: Secondary aerosol formation mechanisms in polar areas by direct measurement of cluster chemical composition and condensing vapours

Jaeseok Kim: Characteristics of New Particle Formation at the King Sejong Station, Antarctic Peninsula

Tuija Jokinen: Solar eclipse – Nature’s own nucleation experiment

Ville Vakkari: Rapid secondary aerosol formation in savannah and grassland fire plumes in southern Africa

Tuomo Nieminen: Global analysis of continental boundary layer new particle formation based on long-term measurements

Christina Williamson: Constraining nucleation mechanisms in global models with measurements of the global distribution of newly formed particles from the NASA Atmospheric Tomography Mission
SECONDARY AEROSOL FORMATION MECHANISMS IN POLAR AREAS BY DIRECT MEASUREMENT OF CLUSTER CHEMICAL COMPOSITION AND CONDENSING VAPOURS

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Keywords: CLUSTER, NUCLEATION, MASS SPECTROMETRY.

INTRODUCTION

Formation of new aerosol particles from trace gases is a major source of cloud condensation nuclei (CCN) in the global atmosphere (Dunne et al., 2016). Controlled laboratory experiments have recently provided detailed, molecular level insight into different nucleation pathways (e.g. Kirkby et al., 2011 and subsequent work performed in CERN CLOUD experiment) but molecular steps and compounds involved in real atmospheric nucleation have been resolved only in very rare locations (Sipilä et al., 2016; Bianchi et al., 2016). Secondary aerosol formation is particularly important in the Arctic and Antarctic atmospheres with low anthropogenic aerosol emissions. Here, we summarize our recent observation of molecular steps of new particle formation from Antarctica and from Arctic polar areas.

METHODS

Field experiments were performed in Queen Maud Land, Antarctica (Nov 2014 – Feb 2015) and at Villum Research Station, Station Nord (Feb - Aug 2015), northern Greenland. Both campaigns utilized an Atmospheric Pressure Interface – mass spectrometer (API-TOF) for measuring the chemical composition of ion clusters and a nitrate ion based Chemical Ionization API-TOF mass spectrometer for measuring the chemical composition of neutral clusters as well as concentrations of low volatility particle precursor vapours, such as sulphuric acid, methane sulphonic acid, iodic acid (Sipilä et al., 2016) and highly oxidized extremely low vapour pressure organic compounds, ELVOC (Ehn et al., 2014). Particle Size Magnifier (PSM), Neutral cluster and Air Ion Spectrometer and a Differential Mobility Particle Sizer (DMPS) were used for measuring the particle size distributions between ca. 1.3 and 800 nm in diameter.

RESULTS AND CONCLUSIONS

Several NPF events, showing the formation of nucleation mode particles and their further growth, were during the Antarctic campaign (Fig. 1). Air mass trajectory analysis revealed that the NPF events occurred only under marine air masses. During the NPF events, relatively high concentrations of sulphuric acid, likely originating from the oxidation of dimethyl sulphide, were observed. Methane sulphonic acid and iodic acid (HIO₃) were also detected but with lower concentrations. Measurements revealed the also the chemical composition of freshly nucleated clusters and their further growth mechanism to climatically relevant sizes.
Several NPF events were recorded also in Northern Greenland. There, at least two different type of cluster formation mechanism were observed. First mechanism was likely related to iodine emissions from sea ice, subsequent gas phase conversion of molecular iodine to iodic acid and iodic acid homogeneous nucleation and possibly subsequent restructuring to I$_2$O$_3$ (Figure 2) (Sipilä et al., 2016). The other mechanism was likely connected to emissions from the open, ice free, ocean. Results from both sites will be presented in detail during the conference.

![Image](image1.png)

Figure 1. New particle formation event recorded by a DMPS in Antarctica in early January 2015.

![Image](image2.png)

Figure 2. Example mass spectrum of iodic acid clusters recorded at Villum Research station, Station Nord in spring 2015. Mass defect describes the difference between the measured mass (in Da) and the sum of nucleons in the atomic nuclei of the clusters and, together with the cluster mass, unambiguously reveals the atomic composition of the clusters. Area of the dot is related to the observed signal strength. For clarity, only the iodic acid and iodine oxide clusters are depicted.

ACKNOWLEDGEMENTS

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REFERENCES


INTRODUCTION

Atmospheric aerosol particles are emitted from natural and anthropogenic sources (i.e., primary aerosol particles) and generated from gas-to-particle conversion processes (i.e., secondary aerosol particles). Nucleated aerosol particles and grown particles can influence radiative balance by scattering and/or absorbing of incoming light and by acting as cloud condensation nuclei (CCN). There are the largest uncertainties in the radiative forcing due to the indirect aerosol effect (IPCC 2013). In particular, effect of new particle formation (NPF) in the atmosphere on climate does not fully understand. A main goal of this study is to investigate characteristics of aerosol particles during the NPF at the King Sejong Station in the Antarctic Peninsula. The changes in aerosol number concentrations and aerosol size number distribution were determined for the identification of NPF events and estimation of formation and growth rate for nucleated nanoparticles. In addition, analysis of air mass back trajectories also was examined to compare properties of NPF depending on the origin and pathway of air masses.

METHODS

Measurement site and instruments

Observations of physical properties of aerosol particles have been conducted at the King Sejong Station (KSJ, 62.22°S, 58.78°W) since March 2009. The KSJ is located on the Barton Peninsula of King George Island, Antarctic Peninsula. Because there are also eight other permanent stations in King George Island, the population density is higher than other stations in Antarctica. The observatory is situated at a distance of about 400 m southwest from the main building of the KSJ including power generator and garbage incinerator. The northeastern direction (355°-55°) was designated as the local pollution sector due to the emissions from the power generator and crematory. The Antarctic Specially Protected Area (ASPA, Narebski Point; ASPA-171) is located approximately 2 km south from the observatory. There are a lot of number of Gentoo and Chinstrap penguins and several birds during austral summer period. In this study, because we focus on understanding of characteristics of the new particle formation (NPF) from natural
sources, we discarded data from the local pollution sector and when black carbon concentrations were higher than 100 ng m\(^{-3}\) to eliminate effect of anthropogenic source on the NPF.

Total number concentrations of aerosol particles were measured with two condensation particle counters (CPC; TSI 3776 and TSI 3772) with 1 Hz time resolution. Based on data from CPC, we investigated total number concentrations of aerosol particles with diameter larger than 2.5 nm (CN\(_{2.5}\)) and 10 nm (CN\(_{10}\)). The difference between CN\(_{2.5}\) and CN\(_{10}\) (CN\(_{2.5-10}\)) values should be used to determine characteristics of nanoparticles produced from gas-to-particle conversion processes and after growth. Sample flow rate of CPC 3776 and CPC 3772 was 1.5 lpm and 1.0 lpm, respectively. Aerosol size number distributions of aerosol particles with a diameter from 10 nm to 300 nm also were determined with a scanning mobility particle sizer (SMPS) consisting of a differential mobility analyzer (DMA), a CPC (TSI 3772), a control unit, an aerosol neutralizer (soft x-ray), and a data logging system. To understand physical properties of Antarctic aerosol particles excluding anthropogenic aerosol, in addition, the aethalometer (Magee scientific, AE 16) was used for measuring the concentrations of light absorbing particles with 880 nm wavelengths. The sample flow rate was 5.0 lpm. A laminar flow air sampling system also was used for the sampling of aerosol particles in this study.

Analysis of Air mass back-trajectory using HYSPLIT model

The analyses of air mass back trajectory were performed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al., 2015; http://www.arl.noaa.gov/HYSPLIT.php). For every 6h period, 120-h air mass back trajectories were analysed, ending at heights of 100m, 500m, and 1500m above the ground level of the sampling site. The results where the origin and pathway of the air masses for at least 12 h were similar at three different heights were used for the analysis in this study. Based on this analysis, we have classified the air mass into four sectors according to their origin and pathway: two continental regions (South America and Antarctica) and two oceanic areas (South Atlantic and South Pacific Ocean).

CONCLUSIONS

Table 1 summarizes measured formation rates among various sampling sites. Our results for formation rate (J\(_{2.5-10}\)) of aerosol particles were estimated using data from two CPCs and are compared with those from other sampling sites. J\(_3\) and J\(_{10}\) correspond to the formation rates of 3 and 10 nm particles, respectively. The formation rate varied according to sampling sites. Although the formation rate of aerosol particles in the KSJ is lower than those at coastal and urban sites, result at the KSJ is higher than those observed from other Antarctic stations. We present only preliminary results in this abstract. The detailed experimental conditions and characteristics of NPF at the KSJ will be discussed in the presentation.
<table>
<thead>
<tr>
<th>Sites</th>
<th>Period</th>
<th>Instruments</th>
<th>Formation rates (cm$^3$ s$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syowa (Antarctica)</td>
<td>08/1978 – 12/1978</td>
<td></td>
<td>$J_{30}$</td>
<td>$3.8 \times 10^{-4}$</td>
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<tr>
<td>Dronne C (Antarctica)</td>
<td>12/2007 – 11/2009</td>
<td>DMPS*</td>
<td>$J_{30}$</td>
<td>0.038</td>
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<td>Abon (Antarctica)</td>
<td>01/2010</td>
<td>DMPS</td>
<td>$J_{30}$</td>
<td>0.003 – 0.3</td>
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<tr>
<td>Neumayer (Antarctica)</td>
<td>28/01/2012 – 26/03/2012</td>
<td>SMPS**</td>
<td>$J_{30}$</td>
<td>0.02 – 0.1</td>
</tr>
<tr>
<td>Värtö (Sub-Arctic)</td>
<td>12/1997 – 07/2001</td>
<td>DMPS</td>
<td>$J_{30}$</td>
<td>0.38</td>
</tr>
<tr>
<td>Hyytiälä (Rural)</td>
<td>1996 – 2003</td>
<td>DMPS</td>
<td>$J_{30}$</td>
<td>0.61</td>
</tr>
<tr>
<td>Mace Head (Coastal)</td>
<td>1996 – 1997</td>
<td>Two CPCs*** (TSI 3022 &amp; TSI 3025)</td>
<td>$J_{310}$</td>
<td>$10^2 - 10^4$</td>
</tr>
<tr>
<td>Jungfrunmoch (Remote)</td>
<td>03/1997 – 05/1998</td>
<td>SMPS</td>
<td>$J_{30}$</td>
<td>0.14</td>
</tr>
<tr>
<td>Dresden area (Rural)</td>
<td>1996 – 1998</td>
<td>Two CPCs (UCPC &amp; CPC)</td>
<td>$J_{30}$</td>
<td>110</td>
</tr>
<tr>
<td>King Sejong (Antarctic Peninsula)</td>
<td>03/2009 – 12/2016</td>
<td>Two CPCs (TSI 3772 &amp; TSI 3776)</td>
<td>$J_{25.10}$</td>
<td>$2.36 \pm 0.95$</td>
</tr>
</tbody>
</table>

Table 1. Comparisons of formation rates of aerosol particles among various sampling sites

ACKNOWLEDGEMENTS

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REFERENCES


IPCC (2013), Climate change 2013: The physical science basis, Intergovernmental panel on Climate ChangeRep., 571-740 pp, Cambridge University Press, New York, USA.


SOLAR ECLIPSE – NATURE’S OWN NUCLEATION EXPERIMENT


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KEYWORDS: field measurements, solar eclipse, new particle formation, mass spectrometry

INTRODUCTION

Solar eclipses have provided fundamental opportunities for scientific research. Several expeditions have been organized to study the celestial dynamics and its impacts on nature during eclipses. The most profound outcomes include the confirmation of the existence of planet Mercury in 1631 (Gassendi 1632), the verification of Einstein’s general theory of relativity (Dyson et al. 1920) and the opportunities to study the atmosphere surrounding the Sun (Saito & Tandberg-Hanssen 1973). Photochemistry is crucial for the human existence on Earth. The most vital photochemical process is photosynthesis, which maintains the oxygen levels in the atmosphere, consumes carbon dioxide and supplies energy for living organisms. The Sun also plays an essential role in the cascade of atmospheric chemical reactions and understanding them is crucial for comprehending cloud formation and changing climate.

New particle formation (NPF) is responsible for producing more than half of atmospheric particles, making them extremely important on human health issues and radiative balance effecting the climate (Merikanto et al. 2009). On most of the locations, observed NPF and subsequent particle growth happen only during daytime, highlighting the importance of photochemical reactions in the process (Kulmala et al. 2004). Simultaneously, the concentrations of oxidants such as OH-radical and ozone are linked to photochemical processes and cycles. Clustering seem to be taking place also in the dark but without observed growth (Lehtipalo et al. 2011). Sulphuric acid is the main NPF initiator and it is formed mainly from sulphur dioxide reaction with OH-radicals or Crieege intermediates (Petäjä et al. 2009; Mauldin III et al. 2012; Sipilä et al. 2010). The newly formed particles are suggested to grow bigger in size by condensation of extremely low-volatilic organic compounds (ELVOC) from terpene oxidation (Ehn et al. 2014; Rissanen et al. 2014; Jokinen et al. 2015). These molecules are responsible for a large part of secondary organic aerosol (SOA) (Ehn et al. 2014; Zhang et al. 2015). To current knowledge, ELVOCs are crucial for NPF, and also nitrogen containing ELVOCs have been suggested to be present during NPF events (Kulmala et al. 2013; Jokinen et al. 2014). Before the current study, very little is known on whether and how they are associated with atmospheric NPF.

METHODS

The concentration of gaseous sulphuric acid measured by chemical ionization mass spectrometer (CI-API-TOF) with nitrate ions used as charger ions. The concentration of sample molecules is calculated as following:

\[ [\text{sample}]_{\text{neutral}} = \frac{\text{sample}^+ + \text{sample-NO}_3^-}{\Sigma \text{reagent ions}} \times C \]  

\[ (1) \]

,where \([\text{sample}]_{\text{neutral}}\) is the calculated concentration (in molecules/cm³) of the neutral measured compound e.g. sulphuric acid, sample+ is the measured signal of sample chemically charged sample charged via proton transfer, sample− NO₃ is the measured charged sample signal formed via clustering and C is a calibration
factor. Reagent ions in the equation are the sum of signals from NO$_3^-$, HNO$_2$,NO$_2^-$ and (HNO$_3$)$_2$NO$_3^-$. Calibration is done using a sulphuric acid generator described by Kürten et al., (2012) (Kürten et al. 2012) Calibration factor determined for these measurements was 2.2e10 molecules/cm$^3$.

Ions and neutral particles using the particle size magnifier (PSM), neutral cluster and air ion spectrometer (NAIS) and differential mobility particle sizer (DMPS). All measurements were conducted at the SMEAR II-station in Hytijiiä, Finland. SMEAR II (Station for Measuring Ecosystem – Atmosphere Relations) station is part of four research stations established in Finland to measure the relationship of atmosphere and forest in boreal climate zone (Hari & Kulmala 2005). SMEAR II-station is located in the middle of a boreal forest, surrounded by a homogeneous Scots pine (Pinus sylvestris) population. Areas in the North and North-East are surrounded by small lakes and wetlands.

RESULTS AND DISCUSSION

In here we present the observations where low-volatility precursor molecules were measured during a partial solar eclipse (81% blocked) on 20 March 2015. The day was a sunny, mostly clear-sky day and small amounts of particles started forming during the morning hours, indicating a beginning of NPF. The first observations during the eclipse show a V-shape drop in UV-B radiation and temperature. The sudden alteration on the solar radiation also effects in oxidant production and thus the eclipse gave an excellent opportunity to investigate the importanace photochemistry on the gas-to-particle conversion process. We observed a clear decrease in certain low-volatile compounds measured by the CI-API-TOF. We also detected that the formation of small particles decreased after the source was cut down. After the eclipse, NPF was initiated again with the production of low-volatile compounds, which confirms the strong association of their formation with atmospheric photochemistry. Details of the compounds that participated in the NPF event during the solar eclipse day will be presented after further analysis of the data.

ACKNOWLEDGEMENTS

We thank the tofTools team for providing data analysis tools for mass spectrometer data. We acknowledge the Academy of Finland Centre of Excellence (grant no. 272041), the European Research Council Advanced Grant (ATM-NUCLE, grant no. 227463), ERC Starting Grant (COALA), the European Union’s Horizon 2020 research and innovation programme (ACTRIS-2, grant no. 654109 and the Marie Sklodowska-Curie grant No. 656994), BACCHUS, a fellowship from the Nordic Centre of Excellence CRAICC and the SMEAR II-station personnel for their help during measurements.

REFERENCES


RAPID SECONDARY AEROSOL FORMATION IN SAVANNAH AND GRASSLAND FIRE PLUMES IN SOUTHERN AFRICA

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Keywords: biomass burning, emission factor, secondary aerosol, savannah.

INTRODUCTION

Open biomass burning (BB) is one of the largest sources of reactive trace gases and fine particles into the Earth’s atmosphere. However, the emissions from wild fires and prescribed burns are highly variable depending on vegetation type and combustion phase of the fire (e.g. Janhäll et al., 2010; Yokelson et al., 2011), while there is also large uncertainty associated with their effects on the global climate (Bond et al., 2013). We investigated the emission factors and atmospheric evolution of BB smoke in southern Africa based on nearly six years of continuous measurements at the Welgegund research station in South Africa, where BB plumes are frequently observed (Vakkari et al., 2014).

METHODS

Measurements were carried out at Welgegund, South Africa (26.57°S, 26.94°E, 1480 m above sea level) from 20 May 2010 to 31 December 2015. For this study the most relevant measurements at Welgegund were aerosol particle number size distribution, CO\(_2\), CO, black carbon (BC) with a MAAP and basic meteorological parameters. Submicron particulate mass (PM\(_1\)) was estimated from the number size distribution using a constant density of 1.5 g cm\(^{-3}\).

Using the methodology of Vakkari et al. (2014) we could identify 130 BB plumes over the measurement period. For 86 plumes the location of the fire could be identified from MODIS burnt area and/or SEVIRI fire radiative power observations. For these episodes – a total of 267 hours of in-plume sampling – we estimated the plume age based on local wind speed and direction (Vakkari et al., 2014). For each 10-minute sample in the plumes the excess CO\(_2\), CO, BC and PM\(_1\) (denoted with a Δ) were calculated by subtracting the background concentrations.

For fresh plumes (i.e. estimated plume age < 0.5 h) modified combustion efficiency (MCE) and PM\(_1\) emission factor (EF\(_{PM1}\)) were calculated following Yokelson et al. (2011). MCE increases with increasing flaming fraction in the fire so that an MCE of 0.9 is considered to represent 50% flaming, 50% smouldering combustion and MCE of 1 indicates complete combustion (e.g. Yokelson et al., 2011). For aged BB smoke the ratio of flaming to smouldering was estimated from the ΔBC to ΔCO ratio (c.f. Vakkari et al., 2014): low ΔBC/ΔCO indicates smouldering-dominated combustion and high ΔBC/ΔCO designates flaming combustion. Combination of these parameters allowed us to investigate the effects of burning conditions and atmospheric transport on PM\(_1\) mass in BB plumes, both in daylight and in the dark.
Figure 1. (a) $\text{EF}_{\text{PM1}}$ vs. MCE for fresh ($<0.5$ h) savannah and grassland plumes. (b) Daytime evolution of $\Delta \text{PM1}/\Delta \text{CO}$ for smouldering combustion, i.e. $\Delta \text{BC}/\Delta \text{CO}$ ranging from 0.005 g g$^{-1}$ to 0.01 g g$^{-1}$.

RESULTS

In good agreement with previous studies (e.g. Janhäll et al., 2010; Yokelson et al., 2011) the $\text{EF}_{\text{PM1}}$ was found to be higher by approximately a factor of 3 for smouldering fires compared to flaming combustion (Figure 1a). Accounting for the MCE, the differences between savannah and grassland $\text{EF}_{\text{PM1}}$ were small.

Under daylight conditions fast secondary aerosol formation was observed in savannah and grassland fire plumes (Figure 1b). The secondary aerosol formation was faster in smouldering-dominated plumes, which resulted in an increase by approximately a factor of 3 in $\Delta \text{PM1}/\Delta \text{CO}$ during the first 3-5 hours; previously secondary aerosol from BB emissions has been shown to also increase aerosol particle growth during regional new particle formation events at Welgegund (Vakkari et al., 2015). Only in the 20% most flaming observed plumes the $\Delta \text{PM1}$ to $\Delta \text{CO}$ ratio did not increase during ageing in daylight conditions. In night-time plumes, whether flaming or smouldering, no change was observed in $\Delta \text{PM1}/\Delta \text{CO}$ during the first 3-5 hours, indicating that photochemical reactions are central in secondary aerosol formation in BB smoke.

CONCLUSIONS

Comparison of $\text{EF}_{\text{PM1}}$ from savannah and grassland fires showed very small differences between the vegetation types when the effect of combustion phase is taken into account. Rapid secondary aerosol formation was observed in daytime BB plumes resulting in most of the PM$_1$ from savannah and grassland fires being secondary aerosol after only a few hours of atmospheric transport under daylight conditions. At this point the PM$_1$ yield can vary from 3 g kg$^{-1}$ for flaming combustion to $>30$ g kg$^{-1}$ for smouldering plumes, where initial emissions are higher and also secondary aerosol formation is faster.
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REFERENCES


GLOBAL ANALYSIS OF CONTINENTAL BOUNDARY LAYER NEW PARTICLE FORMATION BASED ON LONG-TERM MEASUREMENTS

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Keywords: aerosols, new particle formation and growth, long-term measurements

INTRODUCTION

Atmospheric aerosols have effects on air quality, human health and even the global climate. One of the largest uncertainties related to global climate change is the magnitude of the cooling effect of aerosols that counteracts the warming effect caused by greenhouse gases (IPCC, 2013). Formation of secondary aerosol particles from precursor vapours is a major source of atmospheric aerosols (e.g. Merikanto et al., 2009), and a subject of active research during the past two decades. Regional events of new particle formation (NPF) have been observed worldwide (Kulmala et al., 2004), but in the literature reports of the seasonality of the NPF related parameters are still rather sparse. This is partly due to the lack of long-term measurement data on atmospheric particle number size distributions (PNSD). In this study we aim to collect a comprehensive and representative data set of atmospheric PNSD measurements.

MATERIAL AND METHODS

The PNSD data for this study were obtained from open databases hosted by the EBAS (ebas.nilu.no) and ARM (www.archive.arm.gov) projects, as well as directly from several research groups running long-term aerosol measurements. The typical Differential Mobility Particle Sizer (DMPS) or Scanning Mobility Particle Sizer (SMPS) instruments setups used in atmospheric long-term measurements have lower detection limits varying between 3 and 10 nm in diameter, and they measure particles at least upto 500 nm. In order to have comparable results between different sites, a common size range of 10–25 nm was used for nucleation mode particles in this study. We have identified 35 measurement sites worldwide where aerosol size distributions have been measured for at least one year (either continuously or in separate campaigns covering a full seasonal cycle). The sites included in this study range from Arctic, polar and remote areas to heavily polluted megacities.

The size distribution data was classified into NPF event, non-event and undefined days according to the guidelines presented by Kulmala et al. (2012). To quantify the NPF events, the formation rates $J_{\text{nucl}}$ of nucleation mode particles (defined here as particles of 10–25 nm in diameter) were calculated based on the measured number size-distribution data, taking into account the losses due to coagulation and the condensational growth of particles out from the nucleation mode. The particle growth rates were calculated by fitting log-normal modes to the measured size-distribution data and following the time evolution of the geometric mean size of the fitted nucleation mode.

RESULTS AND DISCUSSION

Database of the seasonal cycle of parameters related to regional new particle formation at 35 sites worldwide was created. Most of the sites are located in the Northern Hemisphere in Europe and the Arctic area (Figure 1). Regional NPF events were observed at all the sites throughout the year. The average NPF
frequencies ranged from 12% of days during December–February to 31% of days in March–May. The smallest NPF frequencies occurred in the polar areas, and the highest in the African savannah area.

The particle formation rates do not, on average, show large seasonal variation, but there are large differences between different environments. The highest formation rates that are over 1 cm⁻³ s⁻¹ occur inside cities and other anthropogenically heavily influenced areas. In these areas the SO2 concentrations are typically high leading to high concentrations of sulphuric acid, which is one of the key precursor species in atmospheric NPF. On the other hand, the highest particle growth rates do not occur in these same areas of high formation rates, pointing to the decoupling of the mechanisms leading to the initial particle formation and the subsequent growth of the particles.

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REFERENCES


CONSTRaining nucleation mechanisms in global models with measurements of the global distribution of newly formed particles from the NASA Atmospheric Tomography Mission

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Keywords: Aerosol, Nucleation, Global Modelling, New Particle Formation, Remote Atmosphere

INTRODUCTION

Aerosols nucleated in the atmosphere may account for over half of global cloud condensation nuclei (CCN) (Merikanto et al., 2009). The specific mechanisms of new particle formation affect the concentrations and spatial distributions of these particles (Snow-Kropla et al., 2011), both of which affect their influence on climate. However, the relative importance of different particle formation mechanisms remains poorly understood (Westervelt et al., 2014).

We compare contiguous global datasets of nanoparticle size distributions from two sets of around-the-world flights from the NASA Atmospheric Tomography mission (ATom) with output from the GEOS-Chem-TOMAS global chemical-transport model, with online aerosol microphysics run with different aerosol nucleation mechanisms and convective scavenging efficiencies, to understand the relative importance of the different particle formation mechanisms in the atmosphere. The ATom mission focuses heavily on collecting data from remote, under-sampled areas that provide some of the most direct evidence to distinguish between nucleation mechanisms (Kerminen et al., 2010).

METHODS

Aerosol size distributions were measured on two sets of flights of the NASA ATom mission in August 2016 and February 2017. Flights covered the Pacific and Atlantic basins from ~80°N to ~70°S latitude, constantly profiling between 0.2 and ~13km altitude. The DC-8 aircraft was equipped with instrumentation for measuring aerosols and greenhouse, reactive and trace gases. Here we focus on measurements of aerosol microphysical properties.

Size-distributions from 3nm to 3.5µm were measured with a suite of fast-time-response instruments. Two Nucleation Mode Aerosol Size Spectrometers, batteries of five condensation particle counters each, operating in parallel at constant pressure, with cut-offs between 3 and 60nm, measured nucleation and accumulation mode particles. An Ultra-High Sensitivity Aerosol Spectrometer and a Laser Aerosol
Spectrometer from Droplet Measurement Technologies (Cai et al., 2008 and Hegg et al., 2007 respectively) measured particles from 60nm to 1µm, and from 0.15 to 3.5µm respectively. Instruments were calibrated with dioctyl sebacate, ammonium sulfate and limonene ozonolysis product aerosols, with no statistically significant difference in CPC cut-points measured between the different aerosol compositions. Data taken in clouds were removed from the analysis to avoid instrument artifacts.

We use the ATom size-distribution measurements to evaluate the GEOS-Chem global chemical-transport model (www.geos-chem.org) with online TOMAS aerosol microphysics, performing simulations with 2°x2.5° resolution globally. Sulfate, organic, black carbon, sea-salt, and dust aerosols are modelled in 40 size sections spanning diameters of 3 nm to 10 µm, with diagnostic partitioning of aerosol ammonium, nitrate, and water. TOMAS simulates nucleation, condensation, coagulation, size-resolved emissions, dry and wet deposition, and aqueous sulfate chemistry. We currently simulate binary (H₂SO₄+H₂O), ternary (H₂SO₄+NH₃+H₂O) from Napari (2002) scaled by 10⁻⁵, and binary ion-mediated nucleation schemes, and will include new schemes that are suitable for the temperature and concentration ranges of ATom.

RESULTS AND ANALYSIS

Size distribution measurements from ATom reveal a persistent pattern of high number concentrations of nucleation mode particles at high altitude in the tropics, as shown in the left two panels of Figure 1. This pattern is reproduced in the results of the global model using default convective scavenging/transport assumptions and ternary nucleation from Napari et al. (2002) scaled by 10⁻⁵, as shown in Figure 2. Modeled number concentrations match those measured within orders of magnitude at lower altitudes and in the tropical upper troposphere; however, the model tends to over-predict particle number in the upper troposphere at polar latitudes. Comparison of the full size distribution will allow multiple degrees of freedom for evaluating nucleation mechanisms and convective scavenging/transport.

High concentration of nucleation mode aerosol in the tropics at high altitude coincided with low surface area of accumulation-mode particles, a proxy for condensation and coagulation sinks, as shown in the right two panels of Figure 1. The model captures the magnitude, spatial distribution, and difference between the ocean basins of these parameters, as shown in Figure 3.

Figure 1 Longitudinally averaged aerosol measurements from ATom at standard temperature and pressure (STP): number concentration of nucleation mode particles (diameter 3-60nm) over the Pacific (left-most panel) and Atlantic (2nd panel from left), accumulation mode (60-1000nm) dry surface area over the Pacific (2nd panel from right) and Atlantic (right-most panel).
Figure 2 Dry number concentrations of particles with diameters larger than 3 nm, at STP, simulated using GEOS-Chem-TOMAS using default convective scavenging/transport assumptions and ternary nucleation.

Figure 2 Accumulation mode dry surface area simulated using GEOS-Chem-TOMAS using default convective scavenging/transport assumptions and ternary nucleation.

Figure 4 Composite size distribution measurements from all 18 profiles between 20N and 2S during a single flight over the Pacific.
We postulate a mechanism whereby marine or transported tropical continental air is lofted through deep convective clouds, which scavenge existing aerosol, leaving behind air masses with precursors of low-volatility species and low condensation sinks. Nucleation and growth occur as these air-masses exit the top of the cloud. This mechanism was initially proposed by Clarke et al. (2002), based on previous observations over the Pacific.

Average size distributions over this region indicate that these newly formed particles have the potential to become CCN as the air masses descend. This is shown in Figure 4, where a continuous increase mode particle size is seen with decreasing altitude between 12 and 4 km. Therefore, the processes of convective uplift of precursors, effective scavenging of pre-existing surface area, and copious new particle formation at high altitude may influence planetary albedo and radiation balance in the remote atmosphere. Our observations suggest that this process spans from ~30°S to ~30°N, representing half of the Earth’s global oceanic surface area.

CONCLUSIONS

Contiguous global measurements of aerosol size distributions from ATom reveal a pattern of high nucleation mode aerosol concentrations at high altitude over the tropics, coincident with low surface-area concentrations. The major features of this were reproduced by the GEOS-Chem run with a ternary nucleation mechanism and default convection/scavenging. This indicates that aerosol nucleation occurs in convective outflow of clouds in this region, possibly via ternary nucleation mechanisms, and that these particles grow on descent and may influence climate by becoming CCN. Model results for a variety of nucleation mechanisms and scavenging regimes using back-calculated meteorology for ATom flights, will be compared with the full size distributions measured during ATom to assess their relative importance and improve mechanistic understanding of the observed spatial distribution and concentrations of aerosols.

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REFERENCES

SESSION 9:
AEROSOL FORMATION AND GROWTH

Jonathan Duplissy: Molecular understanding of new particle formation within volcanic plumes using flying mass spectrometer

Jussi Malila: Recognising the role of sulphuric acid in atmospheric new particle formation – a short history

Dominik Stolzenburg: Detailed determination of size- and time-dependent growth rates during new particle formation

Merete Bilde: The effect of temperature on formation and properties of SOA from alpha-pinene ozonolysis

Xiuhui Zhang: A "catalytic" effect of glycolic acid on the formation of sulfuric acid-ammonia molecular clusters

Jonas Elm: Molecular understanding of atmospheric new particle formation from sulfuric acid and diamines

Arto Heitto: Modelling the growth of nanosized particles based on ambient organic vapour concentrations

Olli-Pekka Tikkanen: Hygroscopicity of DMA-SA nanoparticles – comparison of measurements to model predictions
MOLECULAR UNDERSTANDING OF NEW PARTICLE FORMATION WITHIN VOLCANIC PLUMES USING FLYING MASS SPECTROMETER

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Keywords: new particle formation, aerosol nucleation, volcanic particles
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INTRODUCTION

Volcanic emissions are one of the major natural sources of particles in the atmosphere. Volcanic particles injected in the atmosphere can act as cloud condensation nuclei (CCN) (Hobbs et al., 1982) or ice nuclei (IN) (Hoyle et al., 2011) affecting the cloud physical and microphysical properties and, consequently, the Earth’s radiation budget causing significant impact on weather and climate. They are also important components for air quality degradation (Schäfer et al., 2011). Different measurement techniques have been adopted to study tropospheric volcanic aerosols including in situ sampling techniques and remote sensing either from ground, from airborne measurements or from satellite. To date only few in-situ measurements of volcanic emissions have been carried out, largely due to difficulties associated with coordinating the measurements in space and time with volcanic eruptions, as well as due to the relatively harsh environment in the vicinity of volcanic plumes.

Previous in-situ measurement studies have reported: a) the occurrence of nucleation and new secondary particle formation (NPF) events within the volcanic plume (Boulon et al., 2011) and b) the presence of larger particles in the range of 2-3 µm in locations far from the respective volcano. The phenomenon is attributed to particle growth and transport processes (Hervo et al., 2012). The latter result of growth process was also confirmed by LIDAR observations (Bukowiecki et al., 2011).

METHODS

In 2016, as part of the CLERVOLC/STRAP project, a series of ground based and airborne based (French research aircraft, ATR-42) measurements were performed around Etna and Stromboli volcanos in Italy. A total of four flights took place over and around Etna and Stromboli on the 14-16th of June. The ATR-42 was equipped with a number of instruments, including: Scanning Mobility Particle Sizer (SMPS) and two Condensation Particle Counters (CPCs) to measure aerosol physical properties. This combination of instruments covered a wide particle size range (3 nm up to 450 nm) allowing the direct detection of freshly nucleated particles as well as their growth process within the plume. Ozone, NOx, SO2, were also measured. In addition a newly develop Xray-API-tof was measuring sulfuric acid concentration. But most importantly, this mass spectrometer allows to monitor new particle formation from a cluster point of view. This is the first time that such instrument is used in an aircraft.
CONCLUSIONS

In this work, we present an overview of the aerosol and gas phase measurements made aboard the ATR-42. Evidence of NPF was observed within the volcanic plume for both Etna and Stromboli. The NPF events coincided with increases in SO$_2$ concentrations. Most importantly, the composition of the molecular clusters involved in the new particle formation will be presented.

Figure 1: Preliminary data for SO$_2$ concentration during flight 14. Both plumes from Etna and Stromboli were investigated during this flight.

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REFERENCES

RECOGNISING THE ROLE OF SULPHURIC ACID IN ATMOSPHERIC NEW PARTICLE FORMATION—A SHORT HISTORY

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Keywords: history of science, new particle formation, nucleation, sulphuric acid

INTRODUCTION

It is now generally accepted that sulphuric acid is the key ingredient for atmospheric new particle formation, not only in the Earth’s atmosphere, but also in those of other terrestrial planets (and satellites). Indeed, the dependence of the observed new particle formation rate on vapour-phase sulphuric acid concentration has been the main concern for many recent studies on the subject. In this context, a reference to the first direct simultaneous measurements of atmospheric sulphuric acid concentration and small (~ 3 nm) particle concentrations (Weber et al., 1996), or to the pioneering works of Aitken (e.g. Aitken, 1881) is often made. However, the connection between sulphuric acid and atmospheric new particle formation has been acknowledged even well before Aitken: here we trace back the historical and natural-philosophical development of the subject. A more detailed discussion is provided in a recent thesis (Malila, 2016) and in a forthcoming article.

HAZES OF TREMBLING EARTH

The strong hygroscopicity of sulphuric acid must have been well known by alchemist, for whom the oil of vitriol was one the key ingredients. Kant (Kant, 1756a) postulated that earthquakes are due to underground exothermic reactions between water and sulphates, pointing out that fumes from such reactions, when reaching Earth’s surface, produce visible haze; already Aristotle (trans. 1931), citing Democritus, had linked earthquakes with the evaporation of (water) vapour from soil and commented that haze is created in such a process. Kant noted that a haze event—that has later been suggested being a Saharan dust episode (Husar, 2000)—was observed in Locarno two weeks before the Lisbon 1775 earthquake (Kant, 1756b). These considerations are the first ones (to our knowledge) depicting the secondary formation of aerosol particles since the dawn of modern science!

Besides earthquakes, volcanic eruptions were—and are—known to produce new particles from condensing vapours. In connection to the widespread dry fog that covered large areas of Europe following the eruption of Laki in summer 1783, Senebier (?) commented that sulphurous smell was observed in connection to the appearance of haze. Thus, even though Kant later started to doubt his own theory of earthquakes on the basis that there might not be enough sulphur available in the Earth’s crust to explain the amount of released energy (Kant, 1802), the idea of connection between sulphuric acid and atmospheric haze remained.

THE GREAT CHEMICAL LABORATORY

Advancement of science of is sometimes hindered by ridiculous issues. When C. S. Rafinesque wrote

We know that... sulphur, muriate of ammonia, &c. can be formed by sublimation of gases... &c.
may be spontaneously combined by a casual meeting or mixture of gaseous emanations. It is not therefore difficult to conceive how dusty particles may be formed in the great chemical laboratory of our atmosphere.

he expressed a viewpoint that most, if not all, people attending this conference would agree on. His publication (Rafinesque, 1821), however, did not see daylight until more than a century later, as the whole first, and last, issue of this journal was censored immediately after printing!\footnote{The fact that this issue was also edited, and also to a large extent authored, by Rafinesque himself, is not surprising, as his scientific legacy remains still somewhat contradictory.}

Aitken (1881) and R. von Helmholtz (1886) made the first controlled experiments on the influence of sulphuric acid on condensation of water using an expansion chamber and a nozzle exhaust, respectively, and noticed the strengthening effect of $\text{H}_2\text{SO}_4$ in the case of heterogeneous condensation of water on pre-existing particles; in the absence of particles, no condensation was observed. This, however, did not prevent Aitken to speculate that

But when the [sulphuric] acid became highly concentrated, the molecular strain would be greatly increased on account of the vapour tension being greatly in excess of that due to the temperature, and it would then seem to be able to condense without the presence of “free surface.”

Again, considerations related to sulphuric acid predate the possibly more obvious considerations, i.e. those of homogeneous nucleation of water vapour: Barus (1893) was first to suggest this based on his own condensation experiments, a suggestion that was soon proven in Wilson’s (1897) well-known experiment. Also Barus acknowledged the importance of sulphuric acid for atmospheric new particle formation—of which he was the first to record long time series of observations—even considering that a single sulphuric acid molecule could act as a condensation nucleus (Barus, 1905), thus pioneering the ‘activation-nucleation’ or ‘nano-Köhler’ hypothesis (Kulmala et al., 2006) by a century.

Aitken (1912) continued to propose that atmospheric new particle formation follows from photolytic oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$, which then together with ammonia and water vapour forms new particles, as already envisioned by Rafinesque. First direct proof on the role of sulphuric acid in the formation of new particles in the atmosphere was provided by Hogg (1939), who noticed that the intermediate air ions in London were composed of what seemed to be aggregates of tiny sulphuric acid clusters.

CONCLUSIONS

From historical perspective, the connection between sulphuric acid and atmospheric new particle formation is akin to the dilemma of chicken and egg, as these have been seen interlinked even well before when the formal distinction of vapour and aerosol was recognised. (Although there have been, and still are, also other theories concerning atmospheric new particle formation (Husar, 2000).) The subject of atmospheric new particle and nucleation studies has a rich history, which is not always recognised by current researchers.

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REFERENCES


Kant, I. (1802). *Physische Geographie*, Band 1, Rink, F.T. (Comp.) (Göbelns und Unzer, Königsberg).


DETAILED DETERMINATION OF SIZE AND TIME DEPENDENT GROWTH RATES DURING NEW PARTICLE FORMATION

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Keywords: initial growth, inverse modelling, DMA-train, biogenic growth

INTRODUCTION

The formation of nanoparticles through gas-to-particle conversion is observed throughout the global atmosphere (Kulmala et al., 2004). Nucleation at the critical cluster size of 1-2 nm is often followed by growth (Kulmala et al., 2013), such that the newly formed particles can be of significant climactic relevance through the aerosol indirect effect. In competition to growth, newly formed particles can get lost to pre-existing aerosol. This effect is most dominant for particles below 10 nm and in many cases prevents newly formed particles to reach larger sizes. Quantification of nanoparticle growth rates below 10 nm are therefore crucial in estimating the impact of new particle formation on the global climate (Tröstl et al., 2016).

Some authors report growth rates from ambient or chamber measurements quantified with the appearance time method (Kulmala et al., 2013; Lehtipalo et al., 2014; Tröstl et al., 2016). Unfortunately, this method cannot resolve details in the size and time-dependencies of the observed growth events. Several attempts have been made in the past to quantify nanoparticle growth rates by solving the aerosol general dynamic equation (GDE) (Lehtinen et al. 2004; Verheggen and Mozurkewich, 2008; Kuang et al., 2012). However, these methods require a high quality of the input data and so far lack detailed intercomparison. Here we present the development of two new inverse modeling procedures, which have been verified by application to simulated size-distributions. Moreover, we applied both methods to experimental data taken at the NCAR biogenic aerosol chamber.

METHODS

We developed an inverse modeling procedure in order to infer size- and time-dependent growth rates from number size-distributions during growth events. The experimental size-distributions, \( n_{\text{exp}}(d_p, t) \), at time \( t \), are used in order to calculate their evolution with an aerosol dynamics module, including the effects of coagulation, dilution and wall losses. The simulated size distribution, \( n_{\text{sim}}(d_p, t) \), at time \( t + 1 \) is then compared to the measured size-distribution at time \( t + 1 \). This procedure is illustrated in Figure 1.

Two calculation methods are then applied in order to infer the remaining and not simulated effect of growth. The TREND-method tracks regions of the number size-distribution. In that sense, both the simulated and the experimental size-distribution are divided into regions containing a fixed fraction of the integrated simulated size distribution. The shift of corresponding regions between the simulated and the measured distribution then yields the growth rate measurement.
On the other hand, the INSIDE-method interprets the change rate of the size-integrated general dynamic equation. Basically it evaluates the growth term \( \frac{dv(t)}{dt} \) appearing in the GDE as shown in Equation 1:

\[
\frac{dN_{so}}{dt} = \left. \frac{dv}{dt} \right|_{v_{\text{min}}} n(v, t)|_{v_{\text{min}}} + \frac{dN_{so,\text{coag}}}{dt} - \int_{v_{\text{min}}} \beta_{\text{wall}}(v) n(v, t) dv
\]

where \( N_{so} \) is the integrated size-distribution above a certain minimum volume \( v_{\text{min}} \). The first term on the right hand side describes growth, the second term coagulation and the third losses to walls or dilution. The latter two can be covered by the simulation. The growth term is then be evaluated at several minimum volumes or corresponding diameters \( d_{\text{min}} \).

Figure 1. Flow chart of the aerosol dynamics module and the determination of size- and time-dependent nanoparticle growth rates. Experimental data generated by a DMA-train (or other sizing instrument) are fed into an aerosol dynamics module, calculating simulated distributions including the effects of wall losses, dilution and coagulation. Comparison of experimental and simulated distributions allow for the quantification of size- and time-dependent growth rates.

RESULTS

Both methods are tested with size-distribution data generated by computer simulation using the SALSA aerosol dynamics model (Kokkola et al., 2008). With the simulated input data we investigate the contribution of coagulation effects, wall losses and dilution in various conditions. Both methods agree nicely over a wide size-range and a broad set of conditions with the input growth rates of the SALSA-model. This is illustrated in Figure 2, where the relative deviation of both methods to the input growth rates are shown for one selected run and time step.

Figure 2. Relative deviation of both analysis methods from the SALSA input growth rates for a selected run.
In general, deviations are mostly smaller than <5% and if several time steps are analysed, they do not show any significant trend of over- or underestimating the input growth rates. The observed small deviations can be explained by the different representations of the PSD within the models. The SALSA model uses a volume based moving average representation, but the analysis methods consider a distribution of the particles within each size bin.

While the TREND-method generally shows less scatter it cannot determine growth rates at all sizes over all times. However, due to the fixed sizes of the regions, it is not as sensitive to low counting statistics as the INSIDE-method, which can yield some significant deviations with evaluations close to the leading edge of the growing size-distribution.

With this verification of the measurement principle, we used both methods to analyze data from new particle formation experiments carried out at the NCAR biogenic aerosol chamber. We investigated the growth dynamics of α-pinene and β-caryophyllene ozonolysis events. To obtain high quality size-distribution data, we used a prototype DMA-train similar to Stolzenburg et al. (2016). The prototype DMA-train consists out of five differential mobility analyzers (DMAs) running in parallel at fixed but distinct voltages and hence sizes. As it includes no scanning procedure, it offers high time resolution and better counting statistics necessary for capturing fast growth events at close to ambient concentrations. The prototype DMA-train was used in combination with a SMPS system and thereby the setup covered the size-range from 2-100 nm.

The size- and time-dependent growth rates determined with the two GDE-based analysis methods were compared to growth rates determined with the widely used appearance time method and show good agreement. Remarkably, our methods provide much more detail of the size and time dependent growth evolution allowing for unique identification of growth mechanisms. Interestingly, for the two systems studied, we found reversed trends of growth rate evolution. While in the case of α-pinene growth is increasing over time, β-caryophyllene ozonolysis shows rapid growth in the very beginning, but then slows down after the precursor has been reacted away. Regarding the size dependence, only minor effects were found above 10 nm in both systems. Below 10 nm, we confirmed that initial growth proceeds slower, indicating a multi-component Kelvin effect due to the production of different condensable low volatility vapors in the ozonolysis of both, the monoterpene and the sesquiterpene.

CONCLUSIONS

We developed two independent methods based on the evaluation of the aerosol GDE to determine in detail size- and time-dependent growth rates from input size distribution data. The methods were tested by analyzing simulated input data with known growth rates and then used for analysis of new biogenic particle formation from α-pinene and β-caryophyllene ozonolysis. Both methods show good agreement with the simulation and the widely used appearance time method on the experimental data. The analysis of the biogenic particle formation revealed the need for precise time- and size-dependent growth rate measurements in the sub-10 nm range, as both systems were highly dynamic. In comparison, the appearance time method could not resolve unambiguously the size-dependence and the time-dependence of both systems at the same time. Both our methods, however, rely on high quality size-distribution data, i.e. high time-resolution, good counting-statistics and well-calibrated absolute particle concentrations. The latest generation of sizing instrumentation is now capable of providing these requirements (Jiang et al., 2011, Stolzenburg et al., 2016). Especially when applied to well-defined chamber experiments of new particle formation, these new analysis methods will boost our understanding of the underlying mechanisms of aerosol growth. Application of these methods to data from the CERN CLOUD experiment (Kirkby et al., 2011) is planned in the near future.

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REFERENCES


THE EFFECT OF TEMPERATURE ON FORMATION AND PROPERTIES OF SOA FROM ALPHA-PINENE OZONOLYSIS

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Keywords: Particle formation, SOA, Low-temperature ozonolysis

INTRODUCTION

Secondary organic aerosol (SOA) is generated in the atmosphere from the oxidation of volatile organic compounds (VOCs) and comprise a major component of atmospheric aerosol mass. Monoterpenes are biogenic VOCs emitted for example from the Nordic Boreal forest (Spracklen et al. 2008) and are considered an important source of SOA in the natural atmosphere. In this work we focus on the monoterpene alpha-pinene. There is an increasing interest in effects of temperature on yield and properties of SOA from alpha-pinene oxidation (e.g. Järvinen et al. 2016) but a lack of information on the chemical composition of SOA formed at different temperatures. In the present work, the effects of low temperatures on the formation and chemical composition of alpha-pinene SOA are elucidated using a newly constructed state-of-the-art cold-room smog chamber at Aarhus University.

METHODS

A series of alpha-pinene dark oxidation experiments were performed in the newly constructed cold-room smog chamber at Aarhus University. The chamber consists of a ~5 m³ Teflon bag situated in a temperature controlled cold-room covering the temperature range -15 to 25 °C (Kristensen et al., 2017). In the current study, dark ozonolysis (~100 ppb) of alpha-pinene (~10 or ~50 ppb) was performed at temperatures of -15, 0, and 20 °C respectively. In addition, temperature ramp experiments were performed to study changes in particle size and composition as a consequence of increasing or decreasing temperatures. In all experiments, particle number and size distributions were monitored using a Scanning Mobility Particle Sizer (TSI) along with Particle Size Magnifier (Airmodus A10). In addition several other instruments were deployed including an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) for elementary composition of the formed SOA. Molecular composition was probed by off-line analysis by an Ultra High Performance Liquid Chromatograph coupled to the electrospray ionization source of a Bruker Daltonics quadrupole Time-of-Flight mass spectrometer (UHPLC/ESI-qTOF-MS). Highly oxidized multifunctional (HOM) molecules were measured using CI-API-TOF (see separate abstract Quéléver et al. 2017).
CONCLUSIONS

Preliminary results show enhanced SOA formation from ozonolysis of alpha-pinene at the low reaction temperatures. In addition, chemical analyses by HR-ToF-AMS and UHPLC/ESI-qTOF-MS show temperature related differences in the elementary and molecular composition of alpha-pinene SOA (Fig. 1). More specifically, ozonolysis of alpha-pinene at low temperature (-15 °C) results in formation of SOA with higher mass fraction of semi-volatile organic acids and less high molecular weight dimer esters compared to SOA formed at 20 °C (Fig. 1A). In addition, HR-ToF-AMS measurements suggest decreased O/C ratio of SOA formed at -15 °C compared to 20 °C (Fig. 1B). These preliminary results indicate how changes in reaction temperature may influence the chemical composition of SOA from alpha-pinene ozonolysis.

ACKNOWLEDGEMENTS

This work was supported by Aarhus University, the Aarhus University Research Foundation, the European Research Council (Grant 638703-COALA), the Academy of Finland Centre of Excellence program (project no. 272041).

REFERENCES


A “catalytic” effect of glycolic acid on the formation of sulfuric acid-ammonia molecular clusters in the atmosphere

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Keywords: glycolic acid, a “catalytic” enhancement mechanism, main growth paths, new-particle formation.

ABSTRACT

Highly oxidized multifunctional organic molecules (HOMs) which span a wide range of low volatilities have been identified to be capable of driving particle formation as well as the initial growth of particles[1]. However, their participation mechanism in the new particle formation still remains largely ambiguous.

Figure 1. Enhancement strength $R$ of GLA as a function of the logarithm of [GLA] from $10^7$ to $10^{10}$ molecules cm$^{-3}$. All the simulations were under the
conditions of $T=218$K and (a) $[N] = 10^9$ molecules cm$^{-3}$, (b) $[SA] = 10^6$ molecules cm$^{-3}$.

![Diagram](image)

**Figure 2.** Main growth paths of the simulated system under the conditions of $T=218$K, $[SA] = 10^6$ molecules cm$^{-3}$, $[N] = 10^9$ molecules cm$^{-3}$ and $[GLA] = 10^9$ molecules cm$^{-3}$. The red flux stands for the paths containing **SA-N**-based clusters while the blue flux stands for the paths containing **GLA** molecules. The blue dots named $G_{\text{number}}$ represent clusters containing **GLA** molecules. The enhancement mechanism of **GLA** to the **SA-N**-based clusters as a “catalyst” are shown in the brief growth paths.

Here we present an investigation into the effect mechanism of the simplest hydroxyl acid, glycolic acid (**GLA**) on sulfuric acid (**SA**) and
ammonia (N) clusters formation. Density Functional Theory (DFT) calculations combined with Atmospheric Cluster Dynamics Code (ACDC) simulations of (SA):\(N_x\)(GLA)\(_y\) clusters (\(y\leq x+z\leq 3\)) system at different temperatures\(^2\) give direct evidence of the enhancement effect of GLA on SA-N particles formation rates.

By performing structural analyses, it is found that the hydrogen bond or the proton transfer between SA and N molecules become stronger when adding a GLA molecule into the SA-N-based clusters, revealing an enhancement effect of GLA on the molecular interactions. The enhancement strength R of GLA presents a negative dependence on temperature, reaching up to two orders of magnitude at 218K. The positive dependence of R on [GLA] and the negative dependence on [SA] indicate a competitive relationship between SA and GLA. We find that the influence of N on R is more complex: it first increases, reaching a maximum value and then decreases with increasing [N] (Figure 1). The main growth paths (Figure 2) of the system were traced at 218K to identify the potential enhancement mechanism of GLA. In the absence of GLA, the main growth paths of the system were found to proceed mainly via collisions with SA or N molecule. Within the corresponding enhancement concentration, GLA was seen to give rise to a different growth path to the formation of some specific SA-N-based clusters. GLA molecule first forms cluster SA-N-GLA, (SA)\(_2\)-GLA, (SA)\(_2\)-N-GLA and (SA)\(_3\)-N-GLA in a variety of ways, and then the generated GLA contained clusters contribute to the formation of SA-N, (SA)\(_2\), (SA)\(_2\)-N and (SA)\(_3\)-N respectively by the evaporation of a GLA molecule. Hence a “catalytic” enhancement mechanism of GLA has been identified where a GLA molecule acts as a mediating bridge to the formation of SA-N-based clusters. The current study focuses on identifying the role of GLA, chosen here to represent low molecular weight and highly oxidized multifunctional organic molecules, in the formation of particles and their initial growth. We demonstrate that GLA presents an enhancement effect on the particles formation of SA-N clusters system, following a “catalytic” enhancement mechanism. Other highly oxidized multifunctional organic molecules with a variety of different functional groups (carbonyl, ketone, ester or carboxyl groups), molecular weights, volatilities and atmospheric concentrations, their roles and the potential participation mechanisms may be somehow different and are also in great need to be further investigated in order to better understand the new-particle formation (NPF).

ACKNOWLEDGEMENTS
The authors are indebted to the Chinese National Natural Science Foundation (21373025, 91544223), and the United States National Science Foundation (CHE-1305427) for support of this research.

REFERENCES
MOLECULAR UNDERSTANDING OF ATMOSPHERIC NEW PARTICLE FORMATION FROM SULFURIC ACID AND DIAMINES

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Keywords: Nucleation, Quantum Chemistry, Diamines and Clusters.

INTRODUCTION

It is widely known that atmospheric bases, such as ammonia and dimethylamine, are important stabilizers of sulfuric acid clusters and promote new particle formation in the atmosphere. The work by Almeida et al. (Almeida, 2013) showed that ppt levels of dimethylamine was able to enhance new particle formation rates more than three orders of magnitude compared to ammonia and was sufficient to explain new particle formation events observed in the ambient atmosphere.

Recent field campaigns performed by Jen et al. (Jen, 2016) showed that atmospheric diamines can be equally as abundant as monoamines (dimethylamine and trimethylamine). At a site at Jefferson Street in Atlanta, diamine concentrations was even found to exceeded monoamines by a factor of 3. As diamines are more basic than monoamines, they could have the potential to form new particles at even lower concentrations than monoamines.

Here we present the molecular interaction between the primary nucleation precursor H$_2$SO$_4$ and diamines.

MODEL SYSTEMS

As a representative diamine we have chosen to study 1,4-diaminobutane (see Figure 1), better known as putrescine (put). Putrescine is a foul smelling diamine which is emitted into the atmosphere by breakdown of amino acids in dead organic material.

![Figure 1: The molecular structure of putrescine. Green = carbon, blue = nitrogen and white = hydrogen.](image)

We study the cluster formation between sulfuric acid and putrescine to establish the role of diamines in atmospheric new particle formation. As a comparison we also study the corresponding clusters consisting of sulfuric acid and ammonia/dimethylamine.
COMPONENTIAL METHODOLOGY

We utilize density functional theory ($\omega$B97X-D/6-31++G(d,p)) to obtain the molecular structure and vibrational frequencies of the clusters. We thoroughly sample the configurational space using a semi-empirically guided sampling technique in order to obtain the best minimum cluster structures. To improve the single point energy of the structures beyond the DFT level, we utilize a high level domain based local pair natural coupled cluster method – DLPNO-CCSD(T). An example of the largest cluster consisting of four sulfuric acid molecules and four putrescine molecules is shown in Figure 2.

![Figure 2: The molecular structure of the (H$_2$SO$_4$)$_4$(put)$_4$ cluster. Yellow = sulfur, green = carbon, blue = nitrogen and white = hydrogen.](image)

We calculate the formation free energies of the obtained clusters and use the values to obtain atmospheric new particle formation rates using the Atmospheric Cluster Dynamics Code (ACDC). Furthermore, using ACDC we examine the growth paths of the clusters in order to obtain a detailed mechanism of how the particles are formed.

CONCLUSIONS

From our calculations the following important trends can be established:

- Putrescine significantly enhances the new particle formation rate compared to ammonia and dimethylamine.
- Ammonia and dimethylamine can at most stabilize two sulfuric acid molecules.
- A single putrescine molecule is able to stabilize sulfuric acid clusters with at least up to four sulfuric acid molecules.

Our findings explicitly show that diamines are important species for the initial steps in atmospheric new particle formation and only a single molecule is required to stimulate the subsequent growth.

ACKNOWLEDGEMENTS

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REFERENCES


MODELLING THE GROWTH OF NANOSIZED PARTICLES BASED ON AMBIENT ORGANIC VAPOUR CONCENTRATIONS

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Keywords: NANOPARTICLE, GROWTH, ORGANIC AEROSOL, SOA

INTRODUCTION

Under certain conditions new particles can be formed in the atmosphere from ambient gases. These newly formed particles are very small in the beginning, only nanometers in diameter, but later on, in favorable conditions, they can grow to climatic relevant sizes. However, the mechanisms related to this growth are still inadequately known.

We studied the growth of newly formed nanosized particles in the atmosphere based on measurements and by using the particle growth model MABNAG. Particle growth was modelled using measurements of organic vapours at Hyytiala measurement station in spring 2014 during new particle formation (NPF) events and the model results were compared to the measured evolution of particle size distribution.

METHODS

MABNAG (Model for acid base chemistry in nanoparticle growth) is a monodisperse particle population growth model, in which the condensation dynamics is combined with particle’s internal acid-base chemistry (Yli-Juuti et al., 2013). The gas phase vapor concentrations and equilibrium vapor concentrations were used to determine the mass flux between gas and particle phase.

The condensing compounds in the model were water, ammonia, sulfuric acid and a number of organic compounds. The inputs for the growth model were the ambient gas phase concentrations of the condensing compounds. Sulfuric acid concentration was measured with HOxROx-CI-APiTOF (Mauldin
et al., 2017 (in preparation)), ammonia concentrations with MARGA (Makkonen et al., 2012) and concentrations of the organic compounds with FIGAERO-HRTof-CIMS (from now on CIMS) (Lopez-Hilfiker et al., 2014; Mohr et al., 2017, submitted). In addition, the meteorological data (relative humidity, temperature and pressure) were used as input for the model, and simulated growth was compared to particle number size distributions measured with Differential Mobility Particle Sizer (DMPS).

The organic compounds were presented in the model with either five or nine model compounds, depending on the simulation, by grouping the compounds measured by CIMS. One group was composed of the compounds identified as dimers (Mohr et al., 2017, submitted) and the rest of the organics were grouped based on their saturation vapor concentrations (C*) using the volatility basis set (VBS) approach by Donahue et al. (2006). The saturation vapor concentrations (C*) for each of the compounds were calculated using the method introduced by Donahue et al. (2011) with temperature dependence presented by Epstein et al. (2010). We used four VBS bins with C* of 10^2, 10^3, 10^4, and 10^5 µg m^3. In each group we included compounds from range 0.5*10^i < C* < 5*10^i µg m^3 (where i = -4, -3, -2, or -1). In addition, all compounds with lower C* than 10^4 were included in C* = 10^4 µg m^3 bin. The compounds with C* higher than 10^4 µg m^3 were neglected, since their contribution to the growth was insignificant. The simulations were performed by either excluding or including the organic compounds that contained nitrogen. In case nitrogen containing compounds were included these compounds were grouped in a separate 4-bin VBS and the total number of organic model compounds was nine.

In this study, we made separate simulations using time-dependent or -averaged vapor concentrations. In both cases, the properties of organic model compounds (molar mass, molar volume, diffusion coefficient) were calculated using concentration weighted averages over each group. For the case with time-averaged concentrations, the gas phase concentrations and ambient conditions were averaged over the duration of each NPF-event. In time-dependent case the input for the model was taken from the measured concentrations, RH and temperature at each time step. For some NPF events, we did not have data for ammonia or sulfuric acid concentrations. In these cases we used day-time (8am to 6pm) averages over the whole measurement period. Sulfuric acid and ammonia accounted for rather small fraction of the growth according to the model, and, therefore, this assumption is expected to cause relatively small uncertainty in the results.

The model simulations were initialized with a particle that contained 40 sulfuric acid molecules and corresponding water and ammonia according to their gas-particle equilibrium constrained by ambient gas phase observations.

RESULTS

Figure 1 shows the modelled growth of a particle for –average and time-dependent cases together with the measured particle size distribution for one NPF event. As can be seen from the figure, for 29.4.2014, both simulation cases overestimated the growth somewhat, as was the case for most of the NPF events in spring 2014. Most of the particle growth was due to the organic compound with lowest C*, with its mass fraction varying between the NPF events from 70 to 80% and 50 to 60% in simulations without and with nitrogen containing compounds, respectively. We performed the model simulations assuming the organics to be either strong or weak acids, or non-reacting compounds, and the changes between these simulations were insignificant. Also assumptions on whether the organics were di- or monoacids had an insignificant effect on the simulated particle growth.
The sensitivity of simulated particle growth to various factors was also tested. The sensitivity of the simulated particle growth to uncertainties in concentrations of ammonia or sulfuric acid was low, as their contribution to particle mass increase in general was quite small. The uncertainty in the assumed particle and compound properties, such as particle density and saturation vapor concentration of the organics, did have some impact on the predicted particle growth and could impact the quantitative results, although the qualitative results seem reliable.

![Modelled evolution of particle size for time-dependent (green line) and –averaged (blue line) cases and the measured particle number size distribution on 29.4.2014.](image)

**CONCLUSIONS**

Applying the vapor concentrations measured by CIMS in a particle growth model and grouping the organic compounds by VBS approach reproduced the observed growth of particles quite well for spring 2014 in Hyytiälä. The growth was usually somewhat overestimated suggesting that the detected gas phase organics are abundant enough to explain the particle growth. According to the model, the majority of the particle mass increase was due to the low-volatile compounds and, consequently, the predicted growth was not particularly sensitive to uncertainties in the estimated organic vapor pressures. The nitrate containing compounds were predicted to account for a significant (approximately 27-40% by mass) fraction of the particle growth.

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**REFERENCES**
Epstein S. A., I. Riipinen and N. M. Donahue (2010). A Semiempirical Correlation between Enthalpy of
748.
Lopez-Hilfiker F. D., C. Mohr, M. Ehn, F. Rubach, E. Kleist, J. Wildt, Th. F. Mentel, A. Lutz, M.
Hallquist, D. Worsnop, and J. A. Thornton (2014). A novel method for online analysis of gas and
particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols
Semi-continuous gas and inorganic aerosol measurements at a Finnish urban site: comparisons
with filters, nitrogen in aerosol and gas phases, and aerosol acidity, *Atmos. Chem. Phys.*, **12**, 
5617–5631.
Rissanen, H. Liqing, S. Schobesberger, M. Kulmala, R. L. Mauldin III, U. Makkonen, M. Sipilä,
T. Petäjä, J. A. Thornton (2017). Ambient observations of dimers from terpene oxidation in the
gas-phase: implications for new particle formation and growth, Manuscript submitted for
publication.
Yli-Juuti T., K. Barsanti, L. Hildebrandt Ruiz, A.-J. Kieloaho, U. Makkonen, T. Petäjä, T. Ruuskanen,
M. Kulmala, and I. Riipinen (2013). Model for acid-base chemistry in nanoparticle growth
HYGROSOPICITY OF DIMETHYLAMINE-SULFURIC ACID NANOPARTICLES – COMPARISON OF MEASUREMENTS TO MODEL PREDICTIONS


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Keywords: HYGROSOPICITY, DIMETHYLAMINE, SULFURIC ACID, NANOPARTICLES

INTRODUCTION

In order to quantify the global cloud condensation nuclei (CCN) budget we need to develop detailed thermodynamic models and test the predictability of these models by comparing the model output values to measurements. We have studied the hygroscopicity of dimethylamine (DMA)-sulfuric acid (SA) nanoparticles by performing measurements and comparing them to model predictions of a model which has the state-of-the-art amine thermodynamics included.

Sulfuric acid is a known atmospheric nanoparticle constituent whereas different amminium salts have been more recently observed in atmospheric nanoparticles (Smith et al. 2010). Amines are emitted into the atmosphere from anthropogenic and natural sources (Ge et al. 2011a). Theoretical studies have shown that especially dimethylamine enhances the addition of sulfuric acid to nanoclusters containing sulfuric acid and dimethylamine (Loukonen et al. 2010). Besides nucleation, amines can also contribute to the growth of the atmospheric nanoparticles through condensation (Barsanti et al. 2009). These findings imply that accurate representations of the thermodynamics of sulfuric acid-amine systems is needed in order to quantify to which extent nanoparticles grow to CCN sizes.

A previous study on the hygroscopicity of DMA-SA particles has shown that the hygroscopicity of particles close to or larger than 100 nm can be well predicted by the existing theoretical model (Clegg et al. 2013). In this work, we expand our knowledge on the subject to particles smaller than 30 nm in diameter. In the size range studied here, the surface curvature of the particles has a noticeable effect on partitioning of water vapor – a feature for which there exists no model validation results.

METHODS

We studied the hygroscopicity of dimethylamine-sulfuric acid nanoparticles by comparing the hygroscopicity derived from the laboratory measurements to the theoretical values calculated with the state-of-the-art thermodynamical equilibrium model, E-AIM (Wexler & Clegg 2002; Clegg et al. 1998; Ge et al. 2011b).

We prepared five different aqueous DMA-SA solutions with molar DMA:SA ratios of 0.33:1, 0.5:1, 1:1, 3:2 and 2:1 and measured the water uptake of particles at four different relative humidities between ca. 0%-80%. The dry particle sizes selected were 10, 15, 20 and 25 nm. Here we concentrate our analysis to the dry sizes of 10 and 20 nm and to the solution strengths of 0.33:1, 0.5:1 and 2:1.

The nanoparticles were produced by atomizing the aqueous DMA-SA solutions. We measured the hygroscopicity of the particles with a nano hygroscopicity tandem differential mobility analyzer (nano-HTDIMA). Briefly, the nano-HTDIMA is a measurement device which consists of two differential mobility analyzers where the first one is used to select a dry particle size ($D_{dry}$) and the second to scan the size distribution of humidified particles which are counted with a condensation particle counter. The wet diameter ($D_{wet}$) is taken as the mobility diameter where the size distributions peaks and the hygroscopic growth factor (GF) is determined as $GF = D_{wet}/D_{dry}$. 
In addition to the nano-HTDMA measurements, the composition of the produced particles was measured with an Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) from the atomized polydisperse particle population with an approximate mean vacuum aerodynamic diameter at $D_{\text{aero}} = 300 \text{ nm}$. It is notable that the particle sizes from which the composition is measured are larger than the actual particle sizes studied. The implications of this size difference are discussed in the results.

E-AIM is a thermodynamic equilibrium model which calculates the equilibrium partitioning of bulk chemical system given the amounts of different substances which in this work are the amounts of dimethylamine and sulfuric acid in the condensed phase and the relative humidity. To keep the DMA:SA ratio the same during the calculations neither of the substances were allowed to partition into the gaseous phase, meaning that the gas-liquid equilibrium was calculated only for water. E-AIM calculates the equilibrium assuming that the liquid-gas interphase is flat. Hence, the Kelvin correction was applied to the results obtained from the E-AIM. This was done by using the surface tension and density of the solution calculated by E-AIM.

RESULTS

The molar DMA-to-SA ratios of the prepared solutions and the corresponding compositions measured by the HR-TOF-AMS are presented in table 1. For the solutions with molar ratio of 0.33:1 and 0.5:1 the measured composition is more basic than the prepared solution and the solution with molar ratio of 2:1 becomes slightly more acidic. Besides the most basic solution, these results hint that either the sulfurous acid is evaporating from the particles, which seems unlike given it's relatively low equilibrium vapor pressure, or there is a source of DMA vapor in the measurement setup. This source of DMA vapor most likely affects only the composition measurement of the particles since the sampling line leading to the AMS has a residence time of approx. 10 seconds whereas the residence time in the sampling line leading to the nano-HTDMA are only approx. 2 seconds. However, since the molar DMA-SA ratios of the solutions were not measured but rather calculated from the nominal strengths of aqueous DMA and SA solutions, we use the AMS-determined compositions latter. We are currently performing follow-up measurements in order to quantify any possible measurement artifacts.

Table 1: Molar ratio of the solutions and the corresponding nanoparticle composition measured with the HR-TOF-AMS

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<td>0.33:1</td>
<td>0.8:1</td>
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<tr>
<td>0.5:1</td>
<td>1:1</td>
</tr>
<tr>
<td>2:1</td>
<td>1.95:1</td>
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The main results of our work are presented in figures 1 a-b, which show the hygroscopic growth factors as a function of the relative humidity. The markers present the measured values and the lines the modelled ones. Subfigure a corresponds to setup where the particle dry diameter was $D_{\text{dry}} = 10 \text{ nm}$ and subfigure b to dry diameter $D_{\text{dry}} = 20 \text{ nm}$. Different compositions are marked with different colors.

Our results show that the measured hygroscopic growth factors are in every case studied here higher than the GFs obtained from the E-AIM. The relative difference between the measurements and the model is approx. 0%-15%. This difference increases with increasing relative humidity in every studied composition. The discrepancy between the measurements and the model decrease slightly as the particle
size increases. Interestingly, the relative difference is largest in the most basic particles, though the differences with respect to particle composition are only few percent.

![Graphs showing hygroscopic growth factors (GF) of DMA-SA nanoparticles as a function of relative humidity (RH).](image)

**Figure 1**: Hygroscopic growth factors (GF) of DMA-SA nanoparticles as a function of relative humidity (RH). Different colors correspond to different dry particle compositions. Markers represent measured values and the lines values modelled with the E-AIM. Different subfigures represent different dry particle sizes studed.

We also analyzed what would be the DMA:SA molar ratio that would best explain the measured GFs according to E-AIM calculations. This analysis revealed that for the most acidic particles the composition would be around 0.35:1 for the 10 nm sized dry particles and 0.45:1 for the particle with dry size of 20 nm. For all the other studied sizes and DMA:SA molar ratios the composition that best fit to the measurements were between 0.5:1 and 0.8:1.

**CONCLUSIONS**

We measured the hygroscopic growth of the DMA-SA nanoparticles with the nano-HTDMA and found that the measured GFs are higher than the modelled ones in all cases. The relative difference between measured and theoretical values increases with increasing RH and decreases slightly with increasing particle size. The maximum relative difference between measurements and the model is 15%.

The HR-TOF-AMS measured nanoparticle composition differed from that what was expected from the molar DMA:SA ratios of the aqueous solutions. However, given that the predicted and measured composition did not differ more than 3% for the most basic nanoparticles, we are confident our analysis is reliable at least for this composition. Follow-up measurements are needed to confirm the results for more acidic compositions.
Our results hint that the thermodynamics of the SA-DMA-H₂O system might be incorrectly modelled for the systems with noticeable curvature effect. The implications of these findings are that the aqueous phase chemistry and thus the partitioning of different compounds between liquid and gaseous phases might have some uncertainty in the thermodynamic models when the studied system contains DMA.

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REFERENCES


SESSION 10:
ICE NUCLEATION

Anatoly Bogdan: Atmospheric ice nucleation concept hinders the study of high-altitude ice clouds

Paul DeMott: Ice nucleating particle emissions from land surfaces

Ottmar Möhler: A summary of results from the fifth international ice nucleation (fin) workshop series

Christina McCluskey: Abundance and characteristics of ice nucleating particles in remote coastal and oceanic regions

Benjamin Murray: Aircraft measurements of ice nucleating particle concentrations above the dust laden tropical Atlantic

Mikhail Paramonov: A laboratory investigation of the ice nucleation efficiency of mineral and soil dust

Martin Wolf: Probing the Ice Nucleation Potential of Organic Sea Spray Aerosol

Olli Pakarinen: Role of surface structure in heterogeneous nucleation of ice
Atmospheric ice nucleation concept hinders the study of high-altitude ice clouds

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High-altitude ice clouds are upper tropospheric (UT) ice cirrus and ice polar stratospheric clouds (type II ice PSCs). UT ice cirrus clouds cover ~30% of the Earth’s surface, with the larger frequency of occurrence in the tropics$^1$ and, consequently, are important climate regulators. Being globally widespread, they redistribute water vapor (a dominant greenhouse gas) to lower altitudes by the sedimentation of ice crystals, reflect shortwave solar radiation,$^2$ trap terrestrial longwave radiation,$^2$ and supply surfaces for heterogeneous reactions destroying UT ozone,$^3$ an important greenhouse gas at high altitudes. Ice PSCs are culprit of ozone depletion in the winter/spring polar stratosphere$^4$ because heterogeneous chlorine-activation reactions on the surface of cloud particles proceed faster than those in the gaseous phase.$^5$

Ice PSCs and a large fraction of UT ice cirrus are formed in-situ by freezing atmospheric aqueous aerosol drops containing up to 25–30 wt % of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$.$^6$–$^8$ There are works which report that UT aqueous drops may consist of sulfate/organic mixture with a mass fraction even larger than 50 wt %.$^9$ One would expect that atmospheric scientists dealing with high-altitude ice clouds and their impact on the Earth’s climate would have shown an interest to what is going on with solute(s) during the freezing of atmospheric aqueous drops. Unfortunately, over the past several decades, atmospheric scientists ignore the fate of solutes during the freezing of atmospheric aqueous drops i.e., they ignore the physical chemistry of freezing atmospheric aqueous drops. Such attitude to the fate of solute(s) during freezing stems from the fact that atmospheric scientists equate ice nucleation with freezing and, consequently, do not consider the whole freezing process of atmospheric aqueous drops, but focus only on ice nucleation.$^{10,11}$ However, ice nucleation in fact is only the very onset of one and indivisible freezing process which consists of an ice nucleation event and subsequent ice crystallization. A result of such restricted viewpoint on the freezing of atmospheric drops is a generally accepted opinion that ‘atmospheric ice nucleation’ produces pure ice particles.$^{12}$ Therefore, literature,$^{12}$ conferences,$^{13}$ and workshops$^{14}$ are dedicated to ‘atmospheric ice nucleation’. We will name this viewpoint on the
formation of high-altitude ice clouds by the atmospheric ice nucleation concept (AINC).\textsuperscript{10} Currently, the AINC is prevailing in atmospheric science. The main drawbacks of the AINC can be enumerated as follows: (i) the separation of ice nucleation from the whole freezing process, (ii) the equation of ice nucleation with freezing, (iii) the ignoring of the fate of solutes and (iv) prediction of the formation of pure ice crystals.\textsuperscript{10} The current AINC is physically inadequate because, besides the enumerated above drawbacks, it also violates the law of conservation of mass.

![Figure 1](image)

Figure 1. Images of frozen bulk 20 wt % CA (citric acid) (a) and 15 wt % H\textsubscript{2}SO\textsubscript{4} drop (b). FCS means a freeze-concentrated solution which is entangled with an ice framework (IF) or envelop an ice core.

Within the frame of the current AINC, some important problems of the formation and microphysics of UT ice cirrus, for example, the observed elevated ice supersaturation inside UT ice cirrus and low ice crystal number concentration, remain unsolved. The equation of ice nucleation with freezing results in the loss of crucial physical information, namely, a freeze-induced phase separation (FIPS) into pure ice and a freeze-concentrated solution (FCS) which takes place during the freezing of aqueous solutions, including the freezing of atmospheric aqueous drops, Figure 1. In the atmosphere, the FIPS leads to the formation of mixed-phase particles: an ice core enveloped with a FCS coating, not pure ice crystals predicted by the AINC.\textsuperscript{6,8,15-18} Unfortunately, atmospheric ice nucleation community keep ignoring our works dealing with the FIPS in the atmosphere.\textsuperscript{10} Such strange attitude to published works relevant for high-altitude ice clouds may stem from the fact that scientists from the atmospheric ice
nucleation community do not understand the genuine physical chemistry of freezing aqueous solutions. In cryo/biology, biotechnology, pharmaceutics, food industry, tissue engineering etc., FIPS is a well-known and used in technological processes.\textsuperscript{19-21} For example, a freezing step and accompanying FIPS are of large importance in lyophilization/freeze-drying.\textsuperscript{19-21} The aim of this presentation is to present persuasive experimental results, including the visual demonstration (images and movies) obtained \textit{in-situ} during the freezing of aqueous solutions relevant for the atmosphere. We anticipate that they will convince atmospheric ice nucleation community of the importance of FIPS in the atmosphere and, consequently, of the formation of mixed-phase cloud particles. The FCS coating around young UT cirrus particles reduces water vapor uptake and, consequently, hinders the development of UT ice cirrus.\textsuperscript{6,7} The reduced water vapor uptake is responsible for the accumulation and persistence of elevated UT moisture.\textsuperscript{6,7} The FCS coating governs also the rate of heterogeneous reactions destructing UT and polar stratospheric ozone and influence the radiative properties of UT cirrus (absorption, reflection, and scattering of solar and terrestrial radiation). Thus knowledge and utilization of the genuine physical chemistry of freezing aqueous solutions in the study of high-altitude ice cloud is of paramount importance for the proper estimation of the impact of UT ice cirrus on the Earth’s climate and ice PSCs on the ozone depletion and the future recovery of stratospheric ozone budget.

References:


ICE NUCLEATING PARTICLE EMISSIONS FROM LAND SURFACES

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Keywords: ICE NUCLEATING PARTICLES, ICE NUCLEATION

INTRODUCTION

The role of mineral dusts as sources of atmospheric ice nucleating particles (INPs) (Vali et al., 2015), those capable of initiating ice phase transitions, is well known. Nevertheless, laboratory research suggests that mineral dusts cannot explain the abundance of INPs in the atmosphere at higher than a certain cloud temperature, variously reported as -10 to -20 °C. There is evidence that biogenic INPs play a special role in ice formation in supercooled clouds > -20°C (Hoose and Möhler, 2012; Murray et al., 2012). Among biogenic INPs are included plant and soil microbes (and their cell-free INPs), plant fragments, pollen and macromolecules on their surfaces, lichen and unidentified organic INPs enriched in topsoils. Arable soils may represent significant regional sources due to harboring biogenic INPs that include both heat-labile organics of fungal, bacterial and other origin ((O’Sullivan et al., 2014; Fröhlich et al. 2015; Hill et al., 2016) that especially contribute at temperatures higher than about -12 °C, and high heat-stable organics that dominate over included minerals until temperatures below -30°C (Tobo et al., 2014). Active management of these soils predisposes them to being a source of emissions. In previous boundary layer air sampling over agricultural regions, high numbers of heat-labile INPs were detected to dominate INPs as low as -20 °C, even in a period lacking agricultural activities (Garcia et al., 2012). One might posit then that there are additional sources in these regions than from the local soils alone. Here we report on continuing sampling studies being performed over a range of relevant disturbed landscapes/ecosystems present in the Central United States to investigate the presence and action of organic INPs collected from the land surface and in the air above these ecosystems in order to shed light on these varied contributions.

METHODS

Two complementary ice nucleation methods are applied in these studies, one online (real-time) and one offline (post-processing). The CSU Ice Spectrometer (IS) is an offline immersion freezing method applied for aerosols collected onto filters, typically over periods of 2-10 hours in these studies, achieving 800-5500 L sample volumes that extend the range of INP measurements to levels ~0.001 INPs L⁻¹. Aerosols are collected onto 47 mm diameter, 0.2 µm (or 0.05 µm) pore diameter polycarbonate filters fitted within open-faced sterile filter units. During sampling under the perturbations of plant harvesting, a 2.5 µm cyclone (50 % aerodynamic cut-size diameter at 16.7 Lpm, URG Corporation) was sometimes also used, upstream of a 47 mm diameter inline aluminum filter holder (Pall Corporation) fitted with a 0.2 µm pore diameter Nuclepore membrane. Filters and disassembled filter holders were sterilized prior to sampling periods. Processing of samples in the laboratory follow methods detailed in Suski et al. (2017), involving transfer of particles into suspension into 0.02 µm filtered 2 mM KCl (to maintain activity of any K-feldspar), dilution in 2 mM KCl as needed, and distribution of each dilution into an array of 32, 50 µL aliquots within cold blocks in the IS. The samples are cooled from 0 to -27 °C at a rate of -0.3 °C min⁻¹,
and cumulative numbers of INPs per volume of liquid as a function of temperature were estimated following Vali (1971). Values are then converted to concentrations per liter of collected air.

INP concentrations were measured with high time resolution using the CSU Continuous Flow Diffusion Chamber (CFDC) [Rogers et al., 2001; DeMott et al., 2015], operated at 5 % supersaturation with respect to water, and over a temperature range of -15 to -32 °C for closest equivalency to the offline immersion freezing data.

Thermal and chemical (enzyme) treatments are used in this work to discern the contributions of various INP types to the ambient INP concentrations. Post-treatments were applied to the IS filter wash water to selectively deactivate different INP components. To denature labile organic components (e.g., proteins) aliquots are heated to 95 °C for 20 min, while to decompose all organic INPs aliquots were heated to 95 °C in 10% H₂O₂ under UV-B (Suski et al., 2017). Other treatments included digestion with enzymes to lyse all bacteria or proteins (see Hill et al. 2016). Bacterial composition in aerosols was comprehensively profiled (~20,000 sequences for each) using Next Generation sequencing of the 16S rRNA gene amplified from DNA extracted from the aerosol. Upstream of the CFDC a 1-inch diameter quartz tube heated to 300 °C was used to deactivate organic components before they entered the CFDC. By measuring INP concentrations with and without passage through the heating tube, the fraction of organic INPs can be measured in-situ with high time resolution. Laboratory studies using the same soil sample that was bulk-heated by Tobo et al (2014) confirmed the equivalence of this method to bulk heating, and its utility for use in mobile sampling (Suski et al., 2017). Sampling sites have been selected from throughout the U.S. High Plains and Inter-mountain region, including agricultural regions and natural land regions, including grasslands, grazing lands and deserts as shown in Table 1. Ambient air sampling and collection of soil and plant samples for testing their contained INPs has been done at each site using a mobile laboratory that accommodates online and offline INP sampling. Associated real-time measurements of aerosol size distribution and fluorescent biological particles were also made, as described in Suski et al. (2017).

<table>
<thead>
<tr>
<th>Site</th>
<th>Seasons</th>
<th>Ecosystem</th>
<th>Disturbances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamont, OK</td>
<td>Spring</td>
<td>Agriculture (grains)</td>
<td>High wind, rain</td>
</tr>
<tr>
<td>Colby, KS</td>
<td>Fall, Summer</td>
<td>Agriculture (grains)</td>
<td>Harvesting</td>
</tr>
<tr>
<td>Fort Collins, CO</td>
<td>Summer, Fall</td>
<td>Grassland and urban</td>
<td>Wind, fires</td>
</tr>
<tr>
<td>Waverly, CO</td>
<td>Fall</td>
<td>Agriculture (many)</td>
<td>Wind</td>
</tr>
<tr>
<td>Nebraska</td>
<td>Fall</td>
<td>Agriculture (wheat)</td>
<td>Harvesting</td>
</tr>
<tr>
<td>Jelm, WY</td>
<td>Fall</td>
<td>Sagebrush</td>
<td>Wind</td>
</tr>
<tr>
<td>Lingle, WY (SAREC)</td>
<td>Spring, Fall</td>
<td>Agriculture (many)</td>
<td>Harvesting</td>
</tr>
<tr>
<td>Canyonlands, UT</td>
<td>Spring</td>
<td>Semi-arid</td>
<td>Grazing</td>
</tr>
<tr>
<td>Pawnee Grasslands, CO</td>
<td>Spring</td>
<td>Grasslands</td>
<td>Grazing</td>
</tr>
</tbody>
</table>

Table 1. Some sampling sites for INP studies described herein.

RESULTS

Herein we present selected results and summarize those that will be elaborated on in our conference presentation. In the desert region boundary layer sampled for contrast to arable sites, there were smaller contributions of organic INPs (Canyonlands in Figure 1), consistent with the relative absence of organic (abundance of mineral) INPs in the regional soils (not shown). Some grazing regions had high organic INPs, as present in the soils and contributed by the plants in that region (e.g., sagebrush) or transported from surrounding soil and plant-growing regions (e.g., Pawnee Grasslands in Figure 1). Typically, there are more heat labile organic INPs present in the air in all agricultural regions than can be explained by soil sources alone, implying that plant emissions must be considered as distinct sources. Indeed, during times of regional harvesting, sources of labile organic (biological) INPs present on plant tissues raise INP concentrations in the boundary layer to exceptional levels (SAREC in Figure 1) and significant numbers
of bacteria from genera known to contain ice nucleation activity are detected in the air (Figure 2). Results from other sampling scenarios will be shown at the time of the conference.

Figure 1. Figure of Canyonlands (arid inter-mountain, western U.S.) versus U.S. High Plains sites in Colorado (natural grasslands) and Wyoming (corn harvest period).

Figure 2. Diversity and significant potential IN bacterial contribution to aerosol sampled downwind of wheat harvesting near Colby, Kansas. Bacterial diversity was assessed using Next Generation sequencing of the 16S rRNA gene amplified from DNA extracted from the aerosol.

CONCLUSIONS

These continuing studies have demonstrated that INPs from the land surface in natural ecosystems (e.g., grasslands, desert), may reflect transported INPs or be input from local soils and plant emissions at different times. Under very windy conditions or other disturbance, INPs in air appear to reflect soil INP compositions, contributing a dominance of mineral INPs in desert regions (Canyonlands) or heat-stable organic INPs in dry High Plains regions (e.g., Wyoming sagebrush). INPs in air over agricultural regions reflect inputs from local/regional plants (bacteria, fungi and heat labile-organic) and from the underlying arable soils (fungi, heat-stable organics). Strong INP enhancement occurs during local and regional harvesting activities, especially for corn and wheat crops that harbor large numbers of highly active biological INPs, from plant tissues and phylloplane microbes. We have also found (not shown) that INPs during harvesting predominate at sizes above a few microns, so are poorly detected by real-time INP sensors with inlet particle size restrictions. This natural landscape versus agricultural region contrast may provide a window on quantifying emission changes that may have occurred since pre-settlement times.

Quantifying INPs from arable land sources is a multivariate problem that requires emission models for both soil release and a means to specify releases occurring due to agricultural processes in places such as the Central United States. While the soil emissions may presently be included in dust emission models,
providing a link to inclusion of these INP types in global climate models, arable plant and harvesting emissions are not. Results herein suggest the utility of flux studies over an annual cycle at a few representative sites, with sufficient other measurements of aerosol sizes and compositions, including fluorescing biological particles.

ACKNOWLEDGEMENTS

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REFERENCES


A SUMMARY OF RESULTS FROM THE FIFTH INTERNATIONAL ICE NUCLEATION (FIN) WORKSHOP SERIES

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Keywords: Ice nucleating particles, ice residuals, atmospheric aerosols, aerosol mass spectrometry

INTRODUCTION

Primary ice formation by ice nucleating particles (INPs) in clouds contributes one of the largest uncertainties in understanding the Earth’s weather and climate systems. This is related to the poor knowledge of ice nucleation microphysics or of the nature and atmospheric abundance of INPs. During the recent years, new mobile instruments were developed for measuring the concentration, size and chemical composition of INPs, which were tested and intercompared during the three-part Fifth International Ice Nucleation (FIN) workshop series.

The FIN activities continued the series of international collaborative workshops of ice nucleation research (Figure 1), the last one conducted in 2007 (DeMott et al., 2011). The FIN activities not only focused on instrument issues, but also addressed important science topics like the nature of atmospheric INP and cloud ice residuals, the ice nucleation activity of relevant atmospheric aerosols, or the parameterization of ice formation in atmospheric weather and climate models.

![Figure 1. Series of international ice nucleation workshop activities since 1967.](image-url)
FIN ACTIVITIES

The first activity FIN-1 was conducted during November 2014 at the AIDA (Aerosol Interaction and Dynamics in the Atmosphere) cloud chamber (Table 1). It involved co-locating nine single particle mass spectrometers (Aerosol MS) to evaluate how well they resolve the INP and ice residual composition and how spectra from different instruments compare for relevant atmospheric aerosols. We conducted about 90 experiments with mineral, carbonaceous and biological aerosol types, some also coated with organic and inorganic compounds.

The second activity FIN-2 was conducted during March 2015 at the AIDA facility. A total of nine mobile INP instruments directly sampled from the AIDA aerosol chambers. Wet suspension and filter samples were also taken for offline INP processing. A refereed blind inter-comparison was conducted during two days of the FIN-2 activity.

The third activity FIN-3 took place at the Desert Research Institute’s Storm Peak Laboratory (SPL), Steamboat Springs, CO. A selected number of INP instrument was combined with aerosol characterization instruments to study the performance of INP instruments at a remote mountain station field site.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Date</th>
<th>Location</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIN-1</td>
<td>Nov 2014</td>
<td>AIDA</td>
<td>Aerosol MS</td>
</tr>
<tr>
<td>FIN-2</td>
<td>Mar 2015</td>
<td>AIDA</td>
<td>INP instruments</td>
</tr>
<tr>
<td>FIN-3</td>
<td>Sep 2015</td>
<td>SPL</td>
<td>Field site</td>
</tr>
</tbody>
</table>

Table 1. Date and location of the FIN activities. FIN-1 and FIN-2 were conducted at the AIDA facility, KIT Karlsruhe, FIN-3 at the Desert Research Institute’s Storm Peak Laboratory (SPL), Steamboat Springs.

CONCLUSIONS

This contribution will introduce the FIN activities, summarize first results from the formal parts of FIN-1 and FIN-2, and discuss selected scientific results, e.g. the effect of coating on the ice nucleation by mineral aerosols investigated during FIN-1. The coating with both secondary organic compounds and sulphuric acid was conducted in the AIDA chamber at relevant temperatures and precursor concentrations and was monitored with the particle mass spectrometers. Already very thin, atmospherically relevant coatings reduced deposition IN, but had little effect on immersion freezing. Result from the intercomparison of INP instruments and methods from both the laboratory activity FIN-2 and the field activity FIN-3 will also briefly be summarized.

ACKNOWLEDGMENTS

We thank all participants as well as the AIDA and Stormpeak Lab technical teams for a tremendous amount of skillful effort making the FIN workshop series an extremely lively and successful activity of the international ice nucleation community. We also gratefully acknowledge financial support by the U.S. National Science Foundation (NSF grants AGS-1461347 and AGS-1339264), the U.S. Department of Energy (DOE grant DE-SC0014487) and the German Research Foundation (DFG research unit FOR 1525, INUIT).

REFERENCES

ABUNDANCE AND CHARACTERISTICS OF ICE NUCLEATING PARTICLES IN REMOTE COASTAL AND OCEANIC REGIONS


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Keywords: ICE NUCLEATING PARTICLES, MARINE AEROSOL, ICE NUCLEATION

INTRODUCTION

Accurate representation of cloud phase (liquid or ice) in global climate models (GCMs) contributes to large uncertainties in climate projections [e.g., McCoy et al., 2015]. A particularly poorly represented region is the Southern Ocean, where GCMs predict too few clouds that are significantly more glaciated than observations [Kay et al., 2016]. Several factors govern ice phase transitions, including the presence of atmospheric ice nucleating particles (INPs), or particles that initiate heterogeneous ice nucleation. Sea spray aerosol (SSA), generated from wave breaking and bubble bursting at the ocean surface, is an important aerosol source for remote ocean regions and is considered a unique source of INPs [McCluskey et al., 2017]. For a given aerosol number and surface area, lower numbers of INPs are detected in SSA compared to continental aerosol [DeMott et al., 2016], but studies suggest INP emissions can increase due to organic aerosols arising from elevated ocean biological productivity (i.e., phytoplankton blooms). The link between INP emissions and biological activity has been supported through spatial correlations [Schnell and Vali, 1976], measures of IN activity in sea surface microlayer samples collected in the North Atlantic Ocean [Wilson et al., 2015] and direct measures during laboratory mesocosm experiments [e.g., McCluskey et al., 2017]. Furthermore, modeling studies suggest that marine INPs are important for remote regions that are devoid of other INP sources [Wilson et al., 2015]. However, direct evidence for higher ocean-derived INP emissions associated with more biologically productive ocean regions is needed to evaluate model simulations, and this remains a key gap in the scientific understanding of how this potentially important source of INPs contributes to INP populations in remote oceanic regions. Here, we report on recent field campaigns aimed towards surveying natural marine INP number concentrations over oceans, ranging from 65°S to 60°N in the Pacific Ocean. Additionally, we will present recent investigations on the occurrence of increased marine INP emissions due to biological activity in the Southern Ocean and at a remote coastal site on the North Atlantic.
METHODS

Remote marine region data are from the Mace Head Observatory (MHO, Ireland) and six ship campaigns in the Pacific and Southern Oceans, summarized in Table 1. The primary immersion-freezing ice nucleation measurement technique used for these studies is the CSU Ice Spectrometer (IS) [DeMott et al., 2016]. Ambient suspended particles were collected onto filters using open-faced collectors for 4 to 48 hours. The pore sizes of the collection filters were typically 0.2 µm (ship-based) or 0.05 µm (ACAPEX ground-based). Filter samples were shipped frozen to CSU and particles were suspended in pure water for analysis using the IS, providing INP number concentrations (n_{INP}) as a function of temperature (T>-27°C). During the CAPRICORN study, bulk seawater samples were collected (via an oceanography conductivity, depth and temperature (CTD) instrument) and analyzed for number concentrations of ice nucleating entities (n_{IE}) with the IS. An heating test was performed on a portion of the collected aerosol suspension (95°C for 20 minutes) to determine the contribution of heat-labile organic (e.g., protein-containing) INPs. The CSU Continuous Flow Diffusion Chamber (CFDC) [Rogers et al., 2001; DeMott et al., 2016] was used for online detection of n_{IE} onboard the R/V Investigator (CAPRICORN, Table 1). The CFDC was operated in the immersion-freezing mode, at approximately 5% supersaturation with respect to water, and at temperatures ranging from -22 to -32°C.

During ship-based studies, efforts were made to limit aerosol collections to periods that limited contribution from ship emissions. Aerosol size distributions and aerosol composition measurements were also made during each field campaigns and will be used to characterize the contributions of terrestrial aerosol and ship emissions. At the MHO, two aerosol filters were collected daily at the top of a 10-meter mast: “clean sector” and “all sector”. The “clean sector” pump was powered using the MHO Clean Sector Sampler [Rinaldi et al., 2009], which limits sampling to periods of low black carbon concentrations (< 15 ng/m^3) and favorable wind directions (between 180 to 300°). The pump for the “all sector filter” was powered continuously during the total collection period. Thus, clean sector filters correspond to pristine marine aerosol only while all sector filters represent aerosol from both marine and terrestrial sources.

<table>
<thead>
<tr>
<th>Study</th>
<th>Platform</th>
<th>Date</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ship-borne Pole-to-Pole experiment (SHIPPO 2012, SHIPPO 2014)</td>
<td>R/V Araon</td>
<td>July 2012</td>
<td>50°N to 60°N, 44°S to 10°N</td>
</tr>
<tr>
<td>Marine ARM GPCI* Investigation of Clouds (MAGIC)</td>
<td>Horizon Spirit</td>
<td>Jun-Sept 2013</td>
<td>21 to 32°N</td>
</tr>
<tr>
<td>ARM Cloud Aerosol Precipitation Experiment (ACAPEX)</td>
<td>Ron Brown</td>
<td>Jan-Feb 2015</td>
<td>23°N to 38°N</td>
</tr>
<tr>
<td>New Zealand National Institute of Water and Atmospheric Research Southern Voyage (Tangaroa)</td>
<td>R/V Tangaroa</td>
<td>Feb 2015</td>
<td>43°S to 72°S</td>
</tr>
<tr>
<td>Clouds, Aerosols, Precipitation, Radiation, and atmospheric Composition Over the southem ocean (CAPRICORN)</td>
<td>R/V Investigator</td>
<td>March 2016</td>
<td>43°S to 53°S</td>
</tr>
<tr>
<td>Mace Head Observatory (MHO)</td>
<td>Ground Site</td>
<td>Aug 2015</td>
<td>53.3°N, 9.9°W</td>
</tr>
</tbody>
</table>

*Global Energy and Water Cycle Experiment Cloud Systems Study Pacific CrossSection Intercomparison

Table 1. Summary of ship and ground-based measurements used in this study.

RESULTS

Here, we summarize results that will be elaborated upon in our conference presentation. First, we contrast the abundance of atmospheric INPs above oceans from six research voyages conducted to high latitudes from 70°S to 60°N. In general, number concentrations of INPs (n_{INP}) were higher and more variable in the Northern Hemisphere than in the Southern Hemisphere (Figure 1). The n_{INP} observed south of 50°S are the lowest n_{INP} observed in this survey. Aerosol size distributions and composition will be used to evaluate the influence of terrestrial aerosol on ship-based measurements.
At the Mace Head Observatory, \( n_{\text{INP}} \) active at -15°C varied by a factor of over 100 in the all-sector and by a factor of 25 in the clean-sector. Highest concentrations observed in the all-sector were attributed to elevated terrestrial organic aerosol, possibly organic soils. Highest concentrations observed in the clean-sector were associated with a marine organic aerosol event similar to that reported by O’Dowd et al. [2005]. Accordingly, an aerosol mass spectrometer detected elevated mass concentrations of organic aerosol with a corresponding mass spectrum similar to previously observed marine organic aerosol originating from offshore biological productivity [Ovadnevaite et al., 2011]. Furthermore, 72-hour HYSPLIT back trajectory analyses indicated that the marine air originated from the North Atlantic during a period of elevated chlorophyll-a (Chl a). Chl a is a satellite-derived marker for biological productivity.

In addition to evaluating measurements of ambient \( n_{\text{INP}} \), the source strength of the Southern Ocean was evaluated during the CAPRICORN study by investigating the abundance of INEs in seawater samples collected in various locations and depths. Two mesoscale oceanic eddies with contrasting biological productivity were studied extensively by biological oceanographers onboard the R/V Investigator. Analysis of horizontal and vertical profiles of seawater collections from these eddies revealed no correlation between \( n_{\text{INE}} \) and Chl a.

![Graph showing number concentrations of immersion-freezing ice nucleating particles (\( n_{\text{INP}} \)) observed during various ship campaigns in the Southern and Northern Hemispheres, representative of the Pacific and Southern Oceans. Open squares indicate measurements made with the CSU continuous flow diffusion chamber (CFDC). Open circles correspond to \( n_{\text{INP}} \) measured with the CSU Ice Spectrometer (IS).](image)

**CONCLUSIONS**

From six ship-based measurement campaigns, INP number concentrations have been surveyed over the Pacific and Southern Oceans at varied latitudes. These data indicate lower and less variable INP abundance in the Southern Hemisphere compared to the Northern Hemisphere, consistent, from a primary ice nucleation standpoint at least, with its remoteness from terrestrial sources and with the persistence of supercooled liquid clouds in the remote Southern Ocean. In the Southern Ocean, \( n_{\text{INP}} \) reported here are significantly lower than those reported in historical studies [e.g., Bigg, 1973], motivating a careful investigation on the influence of seasonal variability and ice nucleation method comparisons.

Observations of INPs at a well-characterized remote coastal site revealed direct evidence of increased ambient \( n_{\text{INP}} \) that coincided with marine organic aerosol arising from offshore biological productivity. By contrast, the abundance of INEs in seawater revealed a poor relationship between Chl a and the INP.
source strength in the Southern Ocean. Additional biological properties of the mesoscale oceanic eddies will be explored and presented. These measurements illustrate that low INP are common in remote marine environments, and that perturbations, through ocean biological processes and long-range transport, or misrepresentations of INP populations, likely have important implications for ice phase transitions in these regions.

ACKNOWLEDGEMENTS

We acknowledge the Impact of Biogenic versus Anthropogenic emissions on Clouds and Climate: towards a Holistic UnderStanding (BACCHUS) collaborative project for supporting our participation in the Mace Head Study. Partial support for analyses were provided by U.S. National Science Foundation grant AGS-1358495 and U.S. Department of Energy grant DE-SC0014354. The authors wish to thank the CSIRO Marine National Facility (MNF) for its grant of sea time on the R/V Investigator and associated personnel, scientific equipment and data management. We also thank Sebastien Moreau and Peter Strutton (University of Tasmania) for seawater samples collected during the Investigator voyage. We acknowledge Dr. Taehyoung Lee of Hankuk University of Foreign Studies and the Korean Polar Research Institute for conducting SHIPPO collections, and Ernie Lewis for facilitating our participation in MAGIC. We thank Horizon Lines and the Captain and crew of the Horizon Spirit for their support and hospitality during MAGIC. Support for data collected during SHIPPO was provided by the Korean Polar Research Program (PE13410). Measurements during the MAGIC and ACAPEX studies were supported by the Office of Biological and Environmental Research (OBER) of the US Department of Energy as part of the Atmospheric Radiation Measurement Climate Research Facility. Finally, we thank Michael Ritsche, Pat Dowell, Matt Gibson, Mark Smith and Blake Hornblow for their assistance in collecting filters during the MAGIC, ACAPEX campaigns and onboard the R/V Tangaroa.

REFERENCES

AIRCRAFT MEASUREMENTS OF ICE NUCLEATING PARTICLE CONCENTRATIONS ABOVE THE DUST LADEN TROPICAL ATLANTIC

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Keywords: ice nucleation, ice nucleating particle, desert dust, mineral dust.

INTRODUCTION

The formation of ice in supercooled liquid clouds is of fundamental importance for the formation of precipitation as well as cloud lifetime and radiative properties (Tan et al., 2016; McCoy et al., 2015). Mineral dust originating from the world’s arid regions is thought to be one of the most important aerosol types for triggering ice nucleation, not only in locations close to deserts, but also thousands of kilometers from source regions (Hoese et al., 2010; DeMott et al., 2003). The Sahara is the largest single source of atmospheric mineral dust (Ridley et al., 2012; Formenti et al., 2011; Prospero et al., 2002) with ~100 Tg of dust per year exported to the tropical Atlantic and beyond (Kaufman et al., 2005). Despite this region’s dominant contribution to atmospheric desert dust aerosol, very few measurements of the ice nucleating ability of airborne Saharan dusts have been made.

METHODS

In order to make measurements of the Ice Nucleating Particle (INP) spectrum (i.e. the INP concentration as a function of ice-activation temperature) from an aircraft we use a technique originally described and used by Schnell (1982). This technique involves collecting aerosol particles onto filters via inlets located outside the boundary layer of an aircraft and then using a droplet freezing instrument to quantify the density of INPs on the filter. This assay is performed by cooling an array of ultra-pure water droplets placed directly onto the collected filters using a Stirling cryocooler (Whale et al., 2015). Once the density of INPs on the filter is known the concentration of airborne INP particles as a function of activation temperature can be calculated. These measurements were performed as part of the Ice in Clouds Experiment – Dust (ICE-D) campaign conducted out of Cape Verde, Africa, in August 2015. We present the INP concentrations over a range of altitudes from 100 ft (34 m) through to 11,500 ft (3.5 km), sampling air with a wide range of aerosol loadings.

RESULTS AND DISCUSSION

The temperature dependent INP concentration for each filter sample is shown in Figure 1. The measured INP concentrations span more than three orders of magnitude from 10² to 10⁵ m⁻³, over temperatures ranging from about -10 to -25°C. There is also significant variability in the INP concentration at a given activation temperature; for example, at -20°C the INP concentration ranges from about 10³ m⁻³ to 10⁵ m⁻³.

We also compare our n, derived for airborne desert dust with several literature parameterisations. We plot the parameterisation of desert dust n, from a large cloud expansion chamber (Niemand et al., 2012) (referred to as N12 from hereon). This parameterisation is valid between -12 and -36°C, but the bulk of the measurements were below -19°C (the data points from N12 have also been included in Figure 2). The values of n from the N12 parameterisation are larger than the n values for airborne dust over the whole temperature range for both our measurements and those of Boose et al. (2016). The explanation for this discrepancy may be that there is a difference between airborne desert dust and desert dust collected from the surface and then aerosolised for chamber experiments. It has also been noted that there are differences
between different techniques for quantifying ice nucleation (Hiranuma et al., 2015), which might account for these discrepancies. Alternatively, there may be sampling biases associated with the inlet system we used in this study.

Figure 1. Measured ice nucleating particle concentration for all filter measurements during ICE-D.

We also plot K-feldspar $n_s$ parameterisations from Atkinson et al. (2013), Niedermeier et al. (2015) and Peckhaus et al. (2016) (referred to as A13, N15 and P16, respectively). K-feldspar is thought to be the most ice-active mineral in desert dust and typically makes up between 1 and 25% of airborne desert dust mass (Harrison et al., 2016; Atkinson et al., 2013), hence we scale the K-feldspar $n_s$ parameterisations to 1 and 25%, making the assumption that K-feldspar also makes up this fraction of the dust surface area. The A13 parameterisation for K-feldspar provides a good approximation of the slope and magnitude of $n_s$ for most of the filter measurements above about -19°C, but over-predicts the activity at lower temperatures. A minority of the data points sit above the A13 line above -12°C, but these data points make up only ~0.5% of the data points included in the plot and our confidence in these points is therefore low. The N15 parameterisation defines $n_s$ which reaches a limiting value at lower temperatures. However, similarly to the A13 parameterisation, it tends to over-predict relative to the new data for airborne dust. In contrast the recent P16 parameterisation reaches a limiting value at lower $n_s$ values than the N15 parameterisation. The P16 parameterisation is a good predictor of the airborne dust $n_s$ values for both our measurements and that of Boose et al. (2016) below about -19°C, but under predicts $n_s$ at higher temperatures.

While none of the available literature parameterisations fit the $n_s$ values for airborne desert dust across the entire temperature range, it should be noted that the new airborne data is consistent with the various parameterisations within about one to two orders of magnitude. Hence, the laboratory derived parameterisations for desert dust have some skill in predicting $n_s$ for airborne desert dust.
CONCLUSIONS
We have successfully quantified the INP spectrum between about -25 and -10°C for airborne desert dust which was sampled within a few days transport from the African source regions. We also demonstrate that that laboratory-based parameterisations of ice nucleation by desert dust can reproduce the observed values within about one to two orders of magnitude. This suggests that airborne desert dust does not contain a substantial amount of other biological ice nucleating materials active below -10°C, unlike fertile dusts from agricultural sites (O'Sullivan et al., 2016; O'Sullivan et al., 2015; O'Sullivan et al., 2014), and also gives some support to the various laboratory derived INP concentration parameterisations for desert dust. However, significant open questions remain, surrounding the identity and concentration of INPs at temperatures warmer than -10°C, the cause of discrepancies between the different desert dust INP parameterisations and also how desert dust INPs are processed when subject to long range transport.

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REFERENCES


A LABORATORY INVESTIGATION OF THE ICE NUCLEATION EFFICIENCY OF MINERAL AND SOIL DUST

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Keywords: ice nucleation, mineral dust, deposition nucleation, condensation freezing.

INTRODUCTION

Ice nucleation is an important pathway for cloud formation and initiation of precipitation in the atmosphere, thus affecting the Earth’s hydrological cycle and energy and radiative balance (Mülmenstädt et al., 2015). Mineral dust has long been known to efficiently act as an ice nucleating particle (INP), primarily so due to its large size and morphology, and it is commonly associated with the formation of cirrus clouds. Its importance as an INP is increased by its ability to be subject to long-range transport after emission. While the ice nucleating ability of mineral dust increases with its size, there is also a strong dependence on its mineralogical composition, indicating a large and uncertain variability of the ice nucleation activity (INA) of mineral dust from various global sources.

METHODS

Three samples of dust are being investigated with respect to their ice nucleation efficiency. The three dust samples include Iceland glaciogenic silt collected from the glacial river sediments in southern Iceland, China dust collected at a remote location 100 km north-west of Hohhot in China, and Himalaya dust collected in eastern Himalayas at the top of a glacier at an approximate altitude of 5 km. All three dust samples were collected at the surface and, therefore, can be subject to long-range transport.

Submicron size selected (monodisperse) dust samples of 100, 200 and 400 nm in diameter are analysed in the Portable Ice Nucleation Chamber (PINC), an instrument for ice nucleation measurements based on the principle of the Continuous Flow Diffusion Chamber (CFDC) (Rogers, 1988). The measurements of INA are conducted in water sub- and supersaturated regimes to represent deposition nucleation and condensation freezing modes, respectively. The temperature range investigated is 233–248K. In order to investigate the effect of various dust constituents on its INA, three dust treatments were carried out in addition to the untreated samples. These include heating to 573K for 2 hours and treating the samples with H₂O₂ aiming to denature biological proteinaceous matter and digest organic matter, respectively, as well as dissolving the samples in deionised water, which is expected to remove the soluble material.

RESULTS

The results of the experiments with untreated dust samples indicate no significant INA for 100 nm particles at all temperatures and at 248K for all particle sizes. It is found that the INA of dust samples increases significantly between particle diameters of 100 and 200 nm; however, no further significant increase in INA is observed between particles of 200 and 400 nm in diameter. Of the three dust samples examined, China dust exhibits the highest INA for all dust sizes and temperatures, followed by Himalayan and the Icelandic dusts. Preliminary mineralogical analysis indicates that the INA seems to correlate well with the K-feldspar content of the dust samples, particularly microcline, supporting previously published results (Atkinson et al., 2013). As indicated by the calculated ice nucleation active site (INAS) densities,
all three dusts exhibit a non-uniform composition across sizes, i.e. 200 nm particles have more active sites per unit area than 400 nm particles.

The results of the INA activity of the 400 nm untreated and treated dust particles at 243K can be seen in Fig. 1. The heating of samples to 573K for two hours significantly decreased the INA of China and Himalaya dusts in supersaturated regime, indicating the presence of biological proteinaceous matter in these samples; heating had no effect on the INA of Iceland dust. Iceland dust did respond, however, to the washing procedure, where its INA significantly increased following the washing. The likely explanation for this is the presence of the solubile material, the removal of which frees up more active sites on the surface of the dust particles. Washing did not affect the INA of China and Himalaya dusts. The treatment of the dust samples with H₂O₂ resulted in a significant increase in the INA of China and Himalaya dusts, especially in subsaturated regime. The reasons for such behaviour are unknown and are currently under investigation. It is important to note, however, that the dusts that responded to the H₂O₂ treatment are the same dusts that responded to the heating.

As temperature decreased, the effects of the dust treatment became less pronounced, with the measurements at 233K revealing no significant difference in the INA of untreated and treated samples of the same dust (not shown).

![Figure 1. Activated fraction as a function of RH₉ (%) for three dust samples for all treatments. Shown are the mean values with one standard deviation for 400 nm particles at 243K.](image)

CONCLUSIONS

As seen from the complexity of the observed behaviour, it is currently not possible to identify one single particle constituent responsible for the INA of mineral and soil dust. The upcoming work will focus on an in-depth investigation into the reasons behind the observed behaviour of the H₂O₂-treated samples, on improving the mineralogical analysis of the dust samples, as well as on the incorporation of the scanning electron microscopy (SEM), elemental composition and surface area into the overall analysis of the measurements.

REFERENCES


Probing the Ice Nucleation Potential of Organic Sea Spray Aerosol

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Abstract: Sea spray aerosols were generated from cultures of oligotrophic phytoplankton in the genera Prochlorococcus and Synechococcus. Conditions for the onset of ice nucleation were then determined. Organic-enriched particles activated in the deposition mode at supersaturations up to 15% lower than purely inorganic (sea salt) aerosol, which activated in the deliquescent-freezing mode. Only organic containing particles exhibited immersion mode nucleation. Finally, the nucleation of specific classes of marine organic matter was quantified, helping to discern the compounds predominantly responsible for the observed ice nucleation.

I. INTRODUCTION

Marine aerosols comprise one of the most significant aerosol sources on Earth. With total global emissions estimated to be 1–3×1016 g yr−1 (Erikson and Duce, 1998), marine aerosols play pivotal roles in the biogeochemical cycling of nutrients between ecosystems (Duce, 1983). In addition, marine aerosols yield considerable impact on the planetary radiation budget, transporting latent heat across the marine boundary layer (Andreas, 1998) and scattering incoming solar radiation (Bates et al. 2006). This impact is amplified when the ability of aerosol particles to act as cloud condensation nuclei and ice nucleating particles is considered. Marine aerosol particles are often highly hygroscopic, spurring the formation of lower altitude clouds with strongly negative radiative effects (Rossow and Schiffer, 1999). However, highly humid oceanic air often exhibits large convective available potential energies, resulting in updrafts exceeding 10 m s−1 that can eject marine aerosols out of the marine boundary layer (Jorgensen and LeMone, 1989). At these altitudes, marine aerosol particles can activate as ice nucleating particles, forming anvil cirrus that, in contrast to thin cirrus, exhibit a cooling radiative effect over a large geographic area (Carrió et al. 2007).

The ability of marine aerosols to activate as ice nucleating particles is therefore important to quantify. In this study, we focused particularly on the common organic components in marine aerosols, constraining the conditions under which they act as ice nucleating particles in the immersion and deposition freezing modes. Doing so, we generated aerosols from whole-cell and lysed cultures of phenotypically diverse oligotrophic phytoplankton from the genera Prochlorococcus and Synechococcus. These two lineages of cyanobacteria are among the most abundant organisms on Earth and are widely distributed in the world’s oceans, attaining concentrations of up to 2.5×105 and 4.0×104 cells mL−1 of seawater, respectively (Flombaum et al. 2013).

II. SEA SPRAY AEROSOLS

Various empirical source functions have been developed to predict the number and size distribution of aerosol particles as a function of wind velocity at the air-sea interface (O'Dowd and De Leeuw, 2007). Winds in excess of 4 m s−1 induce whitecaps, which directly generate supermicron aerosol particles when their crests break (Figure 1). Breaking waves subsequently entrain bubbles below the surface, scavenging insoluble or semisoluble organic matter as they rise to the surface. This organic matter includes vesicles (Biller et al. 2014), cellular fragments, and molecules released during intercellular signaling, apoptosis, or lysing as a result of predation. At the surface, these bubbles develop a thin film, or cap, that is enriched in organic matter relative to the bulk seawater (Wilson et al. 2015). Fragments of the film are ejected up to 20 cm above the ocean surface as the cap bursts (Blanchard 1963). The void in the ocean’s surface then rapidly fills with seawater, ejecting jet drops that evaporate to
produce particles with radii between 300 nm to 30 μm (Pruppacher and Klett, 2012). Together, the smaller particles from both processes are entrained in the wind, carried beyond the marine boundary layer as sea spray aerosol.

An important feature of the cap-burst versus jet-drop mechanisms is the resulting disparity in chemical composition (Vignati et al. 2010). Particles produced from jet-drops are composed of more soluble organic matter, whole cells or vesicles, and inorganic salts dissolved in seawater. The inorganic fraction includes the major seawater cations: Na⁺ (30.59%), Mg²⁺ (3.68%), Ca²⁺ (1.18%), and K⁺ (1.11%); and major anions: Cl⁻ (55.03%), SO₄²⁻ (7.68%), and HCO₃⁻ (0.41%); where percentages reflect relative molar abundances. The cap-burst aerosols, however, are composed nearly entirely of semisoluble to insoluble organic matter, which includes various carbohydrates, lipids, and proteinaceous molecules and macromolecules.

III. EXPERIMENTAL METHODS

In order to mimic natural sea spray aerosol production, aerosols were generated in the lab using a glass frit bubbler. Filtered air was bubbled through the seawater solution at flow rates that did not disturb the formation of an organic sea surface microlayer. Two axenic (pure) strains of phenotypically distinct high-light adapted ecotypes (HL1 and HLII) of *Prochlorococcus* and one axenic strain of *Synechococcus* (III, 5.1A) were grown to late exponential growth phase in a 13:11 Light:Dark incubator at 24°C. Some cultures were lysed using sonication prior to aerosolization. Aerosols exiting the bubbler were dried in a diffusion dryer and bathed by a steady flow of filtered dry air in a 20 L mixing volume. The particle stream drawn from mixing volume was split, with a portion of the flow (0.35 L m⁻¹) directed towards a condensation particle counter (Brechtel Inc., Hayward CA) that recorded total particle concentrations.

The remainder of the flow (1 L m⁻¹) was directed towards the SPectrometer for Ice Nuclei (SPIN, DMT Inc., Boulder CO), a continuous flow diffusion chamber style instrument. Particles were constrained within SPIN under user-specified temperatures and supersaturations with respect to ice and water. Upon exiting SPIN, particles were recorded as 1) unactivated aerosol, 2) activated cloud condensation nuclei, or 3) activated ice nucleating particles using a multisensory optical particle counter coupled to a machine learning bootstrap-aggregation algorithm (Garimella et al. 2016). Fractional
activation was calculated by comparing SPIN data on ice particle concentration to the total particle concentration obtained from the condensation particle counter.

IV. RESULTS AND DISCUSSION

Based on sizing data from the SPIN optical particle counter, sea spray aerosol with a substantial inorganic component likely deliquesced before nucleating ice. This suggests ice activation occurred on a salty core immersed within a briny solution, akin to deliquescence nucleation. This inorganic SSA activation was constrained to temperatures colder than −38 °C. As illustrated in Figure 2, the supersaturation required to attain 1% fractional activation was nearly indistinguishable for purely inorganic sea spray aerosol as well as aerosols generated from unlysed cell cultures.

Lysing a culture of Prochlorococcus MIT9312 (HLII) proved to decrease the critical supersaturation by 5%. In addition, sea spray aerosol generated from purified Prochlorococcus DNA in seawater activated in the deposition mode at a supersaturation nearly 15% below the supersaturation required for purely inorganic particles. In all tests, fractional activation increased proportionally to the organic content of the sea spray aerosol. In the most notable instances, fractional activation was over 10% higher for sea spray aerosol generated from lysed Prochlorococcus MIT9312 (HLII) than the average fractional activation for purely inorganic SSA.

At temperatures above −38 °C, immersion-mode freezing was observed only for organic-rich sea spray aerosol. Particles composed solely of inorganic components do not nucleate in the immersion mode because the salts dissolve as soon as the particle activates as a cloud condensation nucleus. Particles generated from both whole-cell and lysed Prochlorococcus and Synechococcus cultures, or solutions of organic compounds themselves derived from these cultures, were observed to nucleate in the immersion mode at temperatures as high as −22 °C.

By isolating and testing specific classes of organic compounds, we also probed the ability of proteinaceous, lipid, and carbohydrate-like molecules derived from Prochlorococcus and Synechococcus cultures to initiate nucleation. Lysed cultures were treated with 1) boric acid to esterify saccharide hydroxyl groups, 2) guanidinium chloride and papain to denature and digest proteins, and 3) lipase to hydrolyze the ester groups of bacterial lipids (Pummer et al. 2015). Testing the ice nucleation potential of
particles generated from solutions where the organic content had been restricted to one class of molecules helped to discern the compounds predominantly responsible for the observed ice nucleation.

We conclude that the sea spray aerosol containing organic matter from cosmopolitan cyanobacteria of the *Prochlorococcus* and *Synechococcus* lineages are efficient ice nucleating particles. The inclusion of sea spray aerosol in coupled aerosol-climate models is therefore a crucial step in modeling radiative budgets, particularly for air masses in remote marine regions free from continental influences.

V. REFERENCES


ROLE OF SURFACE STRUCTURE IN HETEROGENEOUS NUCLEATION OF ICE

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Keywords: ICE NUCLEATION, SIMULATION, MOLECULAR DYNAMICS.

INTRODUCTION

An accurate description of clouds in climate models requires solid knowledge about their properties, but formation of ice clouds, in particular, is not well understood. Substances like water do not necessarily freeze when cooled below their thermodynamic freezing point, as the first steps of crystal formation are energetically disfavoured. Crystallization can only proceed once a crystal of critical size has spontaneously formed in the supercooled liquid. The crystal formation barrier is caused by a competition of bulk free energy difference between the phases, favouring the crystalline phase, and an unfavourable component from interfacial energy between the phases. Ice crystals may form in the atmosphere either by homogeneous or heterogeneous ice nucleation. The latter process, where ice formation is initiated by an aerosol seed particle, is active at clearly higher temperatures than homogeneous nucleation. The effect is not thoroughly understood. Different nucleation modes (immersion-, contact- and deposition nucleation) are active in the atmosphere at different temperature and water supersaturation ranges.

METHODS

We have developed an atomistic model of ice crystal formation using a continuum of methods from density functional theory (DFT) to large-scale classical molecular dynamics (MD). We are looking at kinetic and thermodynamic factors controlling nucleation at different conditions and in the presence of different surfaces with varying lattice match with ice, representing aerosol particles. To capture the details of the rare stochastic events of ice nucleation, it is necessary to simulate relatively large systems over long time scales, and therefore classical interaction potentials are used. We utilize the TIP4P/2005 model for water (Abascal and Vega, 2005), as this rigid point charge all-atom model has been shown to reproduce the water phase diagram well and is widely used to study water-ice phase transitions, as well as a computationally cheaper monatomic water model (Molinero and Moore, 2009). Unbiased MD is an ideal method to study realistic physical pathways of ice formation from disordered water requiring collective molecular movement. We employ the DL_POLY_4 (Todorov et al., 2006) and LAMMPS (Plimpton, 1995) codes for parallel MD simulations, where a system including a surface immersed in water is cooled continuously below the melting point over tens of nanoseconds of simulation time and crystallization is followed. Also isothermal simulations are utilized, and we have investigated different nucleation modes including immersion-, contact- and deposition nucleation. We are simulating both ideal test systems with a suitable lattice match, surface corrugation, water-surface interactions, and realistic materials such as different feldspars and AgI that are experimentally found to be active in heterogeneous nucleation, and we show what factors are affecting the nucleation activity.

In addition to studying nucleation dynamics with MD, we are looking at accurate energetics and parameterizing classical interaction potentials between water molecules and surfaces with quantum chemical DFT, utilizing the ORCA code (Neese, 2012) with BP86 functional with D3BJ dispersion. Comparison of water layer adsorption on SiO₂ and graphite versus on K-feldspar is helping us understand the difference in nucleation activity between these materials. We are also utilizing DFT simulations to study water adsorption on hydroxylated graphene, a model for weathered black carbon.
CONCLUSIONS

Flat surfaces with a good lattice match with hexagonal ice nucleates ice effectively at MD time scales (in the order of 10-100 nanoseconds) in immersion mode nucleation, which is regarded as the most important nucleation mode for ice formation in clouds in the atmosphere. Results from mW potential simulations (see Fig. 1.) show that surface geometry alone can explain the high nucleation activity of AgI, whereas K-feldspar, which is considered one of the most important ice nucleation agents in the atmosphere, shows very weak activity in mW simulations for its flat (001) plane. We also study the importance of the effect of feldspar microstructure — the interface between alternating orthoclase and albite layers and defects due to lattice mismatch, as well as other crystal planes such as (100) found important in recent experiments (Kiselev et al., 2017). Contact nucleation mode simulations show nucleation activity at higher temperatures than immersion, in agreement with experiments.

![Figure 1](image)

Figure 1. Surfaces with a good lattice match with hexagonal ice nucleate ice effectively in MD. This result with the monatomic water (mW) potential shows that the high nucleation activity of AgI can be explained by surface geometry alone, without considering specific surface chemistry of the material, whereas for K-feldspar the experimentally observed activity is due to other factors. The inset on the right side of the figure shows the surface geometries of the studied surfaces.

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REFERENCES

Session 11: Ice nucleation

Gregory Schill: The Contribution of Black Carbon to Ice Nucleating Particle Concentrations from Biomass Burning

Robert Wagner: Heterogeneous ice nucleation ability of inorganic sea salt aerosol particles

Daniel Rieger: Scale-dependency of cirrus cloud formation in the icon-art model

Sarah Grawe: Immersion freezing induced by coal fly ash

Atanu K. Metya: Heterogeneous nucleation of supercooled water nano-droplet and droplet containing nanoparticles on rough and smooth surfaces: a molecular dynamics investigation

Daniel Cziczo: Uncertainty in counting ice nucleating particles
THE CONTRIBUTION OF BLACK CARBON TO ICE NUCLEATING PARTICLE CONCENTRATIONS FROM PRESCRIBED BURNS AND WILDFIRES

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INTRODUCTION

Black carbon (BC) has been implicated as a possible ice-nucleating particle (INP) due to its abundance in the upper troposphere (Schwarz et al., 2010). The role of BC as an INP, however, remains unclear. For example, Cozi et al. (2008) report that soot particles were enhanced in the ice phase compared to background aerosol at the high Alpine research station Jungfraujoch; however, future studies at the same site did not see a similar enhancement of BC in ice crystals (Kamphus et al., 2010). Additionally, several aircraft studies have shown that fresh and aged biomass-burning particles influence cloud glaciation (Stith et al., 2011; Twohy et al., 2010), but the specific material responsible for ice nucleation was not definitively determined.

Laboratory results on carbonaceous combustion particles also show conflicting results, especially for laboratory-generated BC particles. Several studies have reported no observable ice nucleation on soot particles within their instrument’s detection limit from -15 to -40 °C (Friedman et al., 2011; Koehler et al., 2009), and suggest that soot particles do not play a significant role in heterogeneous ice formation in mixed-phase clouds. These negative results are in disagreement with a number of previous studies (DeMott, 1990; Diehl and Mitra, 1998), which observed ice nucleation on soot particles at temperatures above -30 °C. These positive results have led to one review article to suggest that BC could potentially rival the importance of mineral dust in mixed-phase clouds below -15 ºC (Murray et al., 2012).

In a similar fashion, current global climate models that incorporate theoretical formulations of heterogeneous ice nucleation often use only the positive laboratory results of ice nucleation on BC and, subsequently, often identify BC as the second-most-abundant INP type after mineral dust (Hoos et al., 2010; Savre and Ekman, 2015). Previous studies have shown that BC from diesel exhaust does not contribute significantly to INP concentrations relevant to mixed-phase clouds (Schill et al., 2016). In contrast, real-world biomass burning events have been shown to be a source of INP (Mccluskey et al., 2014; Prenni et al., 2012) and that BC can contribute to INP concentrations from laboratory burns (Levin et al., 2016). The direct contribution of BC from real-world biomass burning to INP concentrations, however, has not been well defined.

In this paper, we present results from field studies that use a newly developed technique to determine the direct contribution of BC to INP concentrations. Data sets were collected from prescribed burns and from wildfires of opportunity in the Western United States.

METHODS

INP concentrations from biomass-burning events were measured using the Colorado State University continuous-flow diffusion chamber (CSU-CFDC) (Rogers et al., 2001; DeMott et al., 2015), a well characterized thermal gradient diffusion chamber for real-time ice nucleation activity measurements of flowing aerosols.

Additionally, BC measurements were taken with the Single Particle Soot Photometer (SP2). The SP2 uses optical detectors to measure the interaction of individual aerosol particles with a high-intensity 1064 Nd:YAG laser. Those particles that absorb light at 1064 nm, which is primarily refractory BC (rBC)
in the atmosphere, are heated to their vaporization temperature and emit thermal radiation, a process termed laser-induced incandescence. Since the SP2 selectively vaporizes rBC in an aerosol stream, the SP2 can be used as an rBC-specific pre-filter for the CSU-CFDC. Thus, by modifying the SP2 to allow the CSU-CFDC to sample from its exhaust, and by toggling the SP2 laser on and off, the direct contribution of BC to real-world INP concentrations can be determined (Figure 1) (Levin et al., 2014).

The SP2-CFDC was taken into the field to sample from real-world biomass burning events. All measurements were conducted in the CSU Mobile Laboratory (Brown Specialty Vehicles, Lawrence, KS). Prescribed burns were sampled at the Konza Biological Research Station (KBPS, Manhattan, KS), a tallgrass prairie site jointly maintained by the Nature Conservancy and Kansas State University. Furthermore, several wildfires, including the Beaver Creek (Walden, CO), Cliff Creek (Bondurant, WY), and Pioneer (Lowman, ID) wildfires, were sampled in the Western United States.

These results and previous findings of the contribution of BC to INP concentrations in diesel exhaust from Schill et al. (2016) will be input into the Goddard Earth Observing System chemical-transport model (GEOS-Chem). Here, new parameterizations will be made to apply over the model aerosol field outputs in order to determine the potential INP concentrations. Both the potential INP concentration available at the surface as well as the number of INP active as a function of zonally averaged latitude and altitude will be shown. These results will be compared to parameterizations from the previously mentioned positive studies that are often used in models.

![Figure 1. Schematic representation of the CSU-CFDC (a) and the SP2-CFDC (b) techniques.](image)

CONCLUSIONS

Preliminary results of the contribution of rBC to the number concentration of INP ($N_{INP}$) and particles greater than 500 nm in optical diameter ($N_{500}$) are shown in Figure 2. All data sets are normalized to total particle concentrations from a condensation particle counter in order to account for variability in smoke plume concentrations. As shown, rBC often contributes to approximately 20% of $N_{500}$ from wildfires, but does not contribute more than 10% to $N_{INP}$ across all burns. Additional ice nucleation studies, using an offline analysis on filter samples collected during the same prescribed burns and
wildfires, are ongoing. Such techniques are able to determine the contribution of both biological and organic species to INP concentrations by pre-treatment with heat and hydrogen peroxide, respectively (Hill et al., 2016). Comprehensive data, including offline freezing analysis, new parameterizations, and GEOS-Chem outputs will be shown in the conference presentation.

**Figure 2.** The contribution of rBC to INP concentrations ($N_{\text{INP}}$) and particles with an optical diameter greater than 500 nm ($N_{500}$).

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REFERENCES


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HETEROGENEOUS ICE NUCLEATION ABILITY OF INORGANIC SEA SALT AEROSOL PARTICLES

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Keywords: ice nucleation, sea salt aerosol, immersion freezing

INTRODUCTION

In situ measurements of the composition of the residuals of heterogeneously formed cirrus crystals have indicated a significant abundance of sea salt in sampling regions above the ocean (Cziczo et al., 2013). Only recently, independent laboratory measurements have confirmed that inorganic sea salt aerosol (SSA) particles are capable of acting as ice nucleating particles at cirrus temperatures (Ladino et al., 2016; Schill and Tolbert, 2014). The available data, however, are still incomplete in terms of the covered temperature range and the quantification of the ice nucleation efficiency by means of the ice-active fraction and/or ice nucleation active site (INAS) density. We have therefore used the AIDA cloud chamber (Aerosol Interaction and Dynamics in the Atmosphere) to obtain a comprehensive data set for the ice nucleation efficiencies of particles generated from two commercially available sea salt samples (ISS, Instant Ocean sea salt; SA, Sigma Aldrich sea salt) and from a natural Atlantic water (AW) sample in the temperature range from 235 to 200 K.

METHODS

The SSA particles were generated at room temperature by nebulizing 3.5 wt% aqueous solutions of ISS, SA, and the AW sample. As shown in Table 1, the ionic stoichiometry of the three investigated samples was very similar. The nebulized aerosol was dried with two silica gel driers to a relative humidity below 2.5% (dry particle sizes about 0.8 – 0.9 µm) and then injected into the cooled AIDA chamber at temperatures between 235 and 200 K and near-ice saturated conditions.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Instant Ocean Sea Salt (ISS)</th>
<th>Sigma Aldrich Sea Salt (SA)</th>
<th>Natural Atlantic Water (AW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.428</td>
<td>0.420</td>
<td>0.420</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.009</td>
<td>0.010</td>
<td>0.009</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.048</td>
<td>0.049</td>
<td>0.048</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.482</td>
<td>0.488</td>
<td>0.487</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.021</td>
<td>0.025</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Table 1. Ionic stoichiometry of the three investigated samples, expressed as mole fractions of the major components

Upon addition into the AIDA chamber, the SSA particles adopted an internally mixed solid-liquid structure with a brine layer of dissolved inorganic components like e.g. MgSO₄ and KMgCl₃·6H₂O around a solid core of predominantly NaCl (Xiao et al., 2008). The ice nucleation ability of the SSA particles was then investigated in expansion cooling experiments, as conducted by a controlled reduction of the chamber pressure.
RESULTS AND CONCLUSIONS

With increasing relative humidity of the air during an adiabatic expansion in the AIDA chamber, there is a competition between two processes: either full deliquescence of the SSA particles followed by homogeneous freezing, or heterogeneous ice nucleation prior to full deliquescence. Figure 1 depicts time series of the most important AIDA data during two ice nucleation experiments with the AW particles started at 230 K (left part) and 218 K (right part). Panel A shows the AIDA pressure (black line) and gas temperature (red line) during expansion cooling. Pumping is started at time zero. Panel B depicts the ice saturation ratio, \( S_{\text{ice}} \), and panel C the aerosol and cloud particle size distribution (green dots) as measured with an optical particle counter (OPC), as well as the ice-active fraction of the aerosol population (\( f_{\text{ice}} \), blue line). Panel D shows the light-scattering intensity of the particles measured at a scattering angle of 2° (\( I_{\text{sc}} \), black line), as well as the linear depolarization ratio of the particle ensemble, measured at a scattering angle of 178° (\( \delta \), pink line).

Figure 1. Ice nucleation characteristics of AW particles during AIDA expansion cooling experiments started at 230 K (left part) and 218 K (right part). The contents of panels (A) to (D) are explained in the text. Ice nucleation onsets are highlighted by vertical dashed lines.

The experiment conducted at a starting temperature of 230 K displayed an ice formation mode due to homogeneous freezing. The initially mixed solid-liquid AW particles fully deliquesced during expansion cooling and nucleated ice homogeneously at elevated humidity conditions. Full deliquescence was indicated by the observation that the initially small value for the depolarization ratio (4%), which was caused by the undissolved components of the SSA particles, dropped to zero in the course of expansion cooling and only increased again at the onset of ice nucleation (vertical line). The ice nucleation onset was also defined by the appearance of the mode of large particles in the OPC data. In contrast, during the ice nucleation experiment started at 218 K the depolarization ratio did not drop to zero, indicating that the SSA particles still existed in a mixed solid-liquid state at the onset of ice nucleation. This implies that ice formation was due to immersion freezing, which initiated at a much lower supersaturation threshold compared to the homogeneous freezing event shown in the left part of Fig. 1.
Figure 2 summarizes the observed ice nucleation behavior of the three investigated SSA particles (full symbols), showing the temperature-dependent ice saturation ratios needed to initiate ice formation (corresponding to an ice-active fraction of 1%). The open symbols refer to the nucleation onsets reported in previous ice nucleation studies with ISS and SA particles (Ladino et al., 2016; Schill and Tolbert, 2014). The three SSA particle types probed in our experiments displayed a very similar ice nucleation behavior. In summary, the partially effloresced ISS, SA, and AW particles were found to act as ice nucleating particles in the immersion freezing mode at temperatures below about 220 K, with freezing onsets in terms of $S_{\text{ice}}$ between 1.25 and 1.35 for temperatures between 215 and 200 K. Above 220 K, the ISS, SA, and AW particles fully deliquesced and nucleated ice homogeneously. Our measurements thereby confirm that the enhancement of SSA particles found in cirrus ice residue in relation to the background aerosol may be the result of a heterogeneous ice nucleation mechanism.

Figure 2. Ice nucleation onsets of ISS, SA, and AW particles from this study (full symbols) in comparison with previously reported nucleation onsets for ISS and SA particles (open symbols). The black line represents the homogeneous freezing threshold (Koop et al., 2000), the dashed red line is the saturation curve with respect to liquid supercooled water (Murphy and Koop, 2005), and the dashed blue line represents the deliquescence curve for NaCl (Tang and Munkelwitz, 1993).

ACKNOWLEDGEMENTS

We gratefully acknowledge the continuous support by all members of the Engineering and Infrastructure group of IMK-AAF, in particular by Olga Dombrowski, Rainer Buschbacher, Tomasz Chudy, Steffen Vogt, and Georg Scheurig. We thank Luis Ladino for providing the data shown in Fig. 2. The work has been funded by the Helmholtz-Gemeinschaft Deutscher Forschungszentren as part of the program “Atmosphere and Climate” and by the Deutsche Forschungsgemeinschaft (DFG) as part of the Ice Nuclei Research Unit INUIT (FOR 1525, project MO 668/4-2).
REFERENCES


SCALE-DEPENDENCY OF CIRRUS CLOUD FORMATION IN THE ICON-ART MODEL

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Keywords: aerosol, clouds, scale-dependency, parameterization.

INTRODUCTION

Due to horizontal averaging of input variables, the outcome of non-linear physical parameterizations in modelling systems can depend on the horizontal grid spacing. Hence, the result of model simulations can depend on grid spacing. This behaviour has for example been reported for atmospheric chemistry and aerosol dynamics (Weigum et al., 2016), cloud formation (Ma et al., 2015), as well as for precipitation (Barthlott and Hoose, 2015).

For nested simulations, this scale-dependency can create unrealistic gradients at the boundaries even though no differences in the physical parameterizations or numerical methods exist. A common technique to account for this scale-dependent behaviour is to assume a probability density function (PDF) for the subgrid-scale distribution of the input variable, to calculate the process multiple times with different values of the input variable and to generate a weighted result based on the PDF (Ghan et al., 1997; Larson et al., 2001).

Assuming a subgrid-scale distribution can prove very difficult, for example for vertical velocity in the altitude of cirrus clouds. Nevertheless, a good description of this distribution is crucial to calculate ice nucleation. Due to adiabatic cooling, saturation in an ascending air parcel increases, hence vertical velocity is the main source for supersaturation. Depending on the amount of supersaturation, the highly non-linear ice nucleation process differs strongly. In a case study of a Saharan dust event in Central Europe on 3 April 2014, we investigate the impact of grid spacing on the formation of cirrus clouds.

METHODS

We are using the online-coupled modelling system ICON-ART (Zängl et al., 2015; Rieger et al., 2015, ICOsaheDrul Nonhydrostatic - Aerosols and Reactive Trace gases). The host model ICON is used by the German Weather Service (DWD) for numerical weather prediction (NWP) and by the Max-Planck-Institute for Meteorology for climate projections. The ART extension is developed at Karlsruhe Institute of Technology (KIT) in order to take feedback processes between trace substances and the state of the atmosphere into account.

ICON is a global model with a non-hydrostatic dynamical core and an option to include local nests with a refined grid spacing. This is enabled by a Arakawa C type grid based on an icosahedron projected on a sphere resulting in triangular grid elements. By using the nesting technique, one can obtain results at multiple resolutions during one model simulation.

The ART extension includes currently the spatiotemporal evolution of gaseous substances including chemical reactions as well as primary aerosol compounds (mineral dust, sea salt, volcanic ash). Additionally, it includes the interaction of aerosol particles with radiation (Gasch et al., 2017) and
cloud formation (Rieger, 2016; Rieger et al., 2017). The nesting capability of ICON-ART comes in handy for the examination of aerosol-cloud interactions, as for example, the grid can be refined in the source as well as in the target region allowing for a highly-resolved description of the important processes. With this approach, boundary data for the highly resolved areas is still obtained from a consistent modelling system at a coarser resolution avoiding unrealistic gradients at the boundaries due to differences in numerical description or physical parameterizations.

In addition to the operational bulk cloud microphysics scheme with prognostic mass mixing ratios of four hydrometeor species (cloud water, rain, cloud ice, snow), a two-moment microphysics scheme (Seifert and Beheng, 2006) is available with prognostic mass concentrations and number concentrations of six hydrometeor species (cloud water, rain, cloud ice, snow, graupel, hail). Using the ART extension, this scheme is coupled with the cirrus cloud formation parameterization, which accounts for the competition between homogeneous and heterogeneous ice nucleation processes (Barahona and Nenes, 2009).

This study focusses on cirrus cloud formation in Central Europe during a Saharan dust outbreak at 3 April 2014. The simulations are performed on a so-called R2B6 grid with an effective grid spacing of 40 km. A nest with 20 km grid spacing is added covering source (North Africa) as well as target region (Central Europe). Additional nests with 10 km and 5 km effective grid spacing cover the analysis region in Central Europe including Germany, France and adjacent regions. Apart from the advanced scheme for cloud microphysics, the NWP physical parameterization package of ICON is used. In order to achieve a realistic spatial distribution of the mineral dust aerosol, a spinup of in total 19 days is performed, with daily reinitialization of the meteorological fields using ECMWF (European Centre for Medium-Range Weather Forecasts) analysis data at 0 UTC of the five days preceding the analysis period.

CONCLUSIONS

For our simulation of the case study on 3 April 2014, we are assuming a Normal subgrid-scale distribution of the updraft as input for the ice nucleation parameterization. As the mean value of the distribution, we are using the grid scale updraft. The width of the distribution was tuned based on comparisons of the 5 km results with aircraft measurements to \( \sigma = 0.3 \cdot \sqrt{\text{TKE}} \). Although using this PDF approach, we find systematic differences in the mean ice particle concentrations at different resolutions. As illustrated in the top of figure 1, the higher the resolution, the higher is the ice particle number. The slightly higher peak of the 40 km result compared to the 20 km result is caused by an model initialization effect.

To overcome these differences, we developed a method to correct the subgrid-scale distribution function based on the results of the highly resolved simulation. The approach of is this method is that the sum of energy from grid-scale vertical motion (updraft) and subgrid-scale vertical motion (fraction of TKE) should be constant at different horizontal resolutions. However, even after tuning the fraction of TKE that is used for the width of the distribution according to measurements, there is still a residual between the energy at two different resolutions. This residual is caused by an inaccurate TKE representation at different resolutions. This calculated residual however can be used to further tune the simulations. At the bottom of figure 1, the results after this additional tuning are shown. The differences in ice particle number concentration between different horizontal resolutions have decreased significantly.

This method reduces the differences in mean ice particle concentration between the 40 km and the 5 km simulation from 12% to 2%. Hence this method increases ICON-ART’s flexibility to be used over a wide range of spatial and temporal scales.
Figure 1: Mean ice particle number concentration in the analysis domain at heights with $T < 235\,\text{K}$ between 3 April 12 UTC and 4 April 0 UTC for the simulation without (top figure) and with (bottom figure) parameterization (Rieger, 2016).

REFERENCES


IMMERSION FREEZING INDUCED BY COAL FLY ASH: COMPARING PARTICLE GENERATION METHODS AND MEASUREMENT TECHNIQUES

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Keywords: ICE NUCLEATION, FLY ASH.

INTRODUCTION

Ice particles in clouds influence weather and climate, e.g., by affecting precipitation formation and cloud radiative properties. Hence, studying their formation and behavior is important for achieving a better representation of ice related processes in weather and climate models. Ice particles can be formed either by primary mechanisms such as homogeneous and heterogeneous nucleation, or by secondary mechanisms. In the atmosphere, homogeneous nucleation, i.e., the freezing of pure water or solution droplets, takes place at temperatures below -38 °C (Rosenfeld and Woodley, 2000; Koop et al., 2000). At water saturation, this temperature limit of droplet freezing is raised in the presence of ice nucleating particles (INPs) acting as catalysts for ice formation, which is then referred to as immersion freezing. To date, a lot of effort has been put into the identification and characterization of atmospheric INPs. The majority of studies focuses on INPs from natural origin such as biological particles or mineral dust particles (Hoose and Möhler, 2012; Murray et al., 2012). Combustion ashes, being possible sources of anthropogenic INPs, have rarely been investigated in the past. Consequently, the contribution of ash particles to atmospheric ice nucleation is rather unclear. Ash may be emitted into the atmosphere either by the action of wind from ash deposits on the ground (bottom ash), or during combustion processes (fly ash). Two recent studies (Umo et al., 2015; Grawe et al., 2016) identified fly ash particles from coal combustion as being more efficient at nucleating ice than bottom ashes from wood and coal combustion. These results motivated the here presented study in which we investigated the immersion freezing behavior of four coal fly ash samples taken from the filters of different coal-fired power plants in Germany. On the one hand, this study focuses on the quantification of the ice nucleation efficiency of fly ash particles from different origin. On the other hand, we aim at investigating the effect of different measurement techniques on immersion freezing results which can possibly contribute to the overall understanding of such measurements and hence to data quality.

METHODS

A combination of two instruments was used to capture the temperature range from 0 °C to the homogeneous freezing limit. Firstly, the new Leipzig Ice Nucleation Array (LINA; similar to the freezing array described by Budke and Koop, 2015) was used, where 90 droplets from an ash-water suspension, each 1 µl in volume, are placed onto a hydrophobized glass slide on top of a stage cooled by a Peltier element. Starting at 0 °C, the temperature is decreased at 1 K min⁻¹ until all droplets are frozen. The number of frozen droplets is determined with a temperature resolution of 0.1 K by evaluating camera recordings of the experiment. To allow comparability to the freezing array results by Umo et al. (2015),...
the suspensions were produced in the way described therein by mixing dry ash powder with MilliQ water, followed by 10 min in an ultrasonic bath and 24 h of stirring. Secondly, the immersion freezing behavior of the fly ash particles was determined using the Leipzig Aerosol Cloud Interaction Simulator (LACIS; Hartmann et al., 2011). In contrast to LINA, where each droplet contains numerous particles of different sizes, LACIS is a laminar flow tube in which every droplet contains a single ash particle of selectable size. Particles are activated to cloud droplets by creating supersaturation with respect to water via cooling the tube walls and adjusting the inlet dew point. Further cooling towards the outlet of the tube causes a certain fraction of droplets to freeze. This so-called ice fraction $f_{\text{ice}}$ is determined at the outlet with the help of the Thermo-Stabilized Optical Particle Spectrometer for the detection of Ice (TOPS-Ice; Clauss et al., 2013). The LACIS setup gives us the opportunity to investigate the effect of particle generation on immersion freezing. On the one hand, particles were generated by aerosolization of dry ash material (dry particle generation), on the other hand, by atomization of the aforementioned ash-water suspension (wet particle generation). A schematic of the different kinds of particle generation and the experimental setup can be seen in Fig. 1.

![Experimental setup showing LINA and LACIS.](image)

Figure 1. Experimental setup showing LINA and LACIS. Two different kinds of particle generation, wet and dry, were used for the LACIS experiments. The following abbreviations are included: differential mobility analyzer (DMA), condensation particle counter (CPC), ultra-high sensitivity aerosol spectrometer (UHSAS), aircraft-based laser ablation aerosol mass spectrometer (ALABAMA), dew point mirror (DPM), thermostat (TH).

For a better comparability between LINA and LACIS, the measured $f_{\text{ice}}$ values were converted into ice nucleation active surface site densities $n_s$ by taking the INP surface area into account. In the case of LACIS we assumed spherical particles with the diameter being the mobility diameter selected by the DMA. For LINA, a total surface area was calculated based on the amount of material in each droplet and the specific surface area derived from nitrogen adsorption measurements (BET).
RESULTS

Fig. 2 shows the results of the LACIS measurements. The $f_{\text{ice}}$ values for particles from dry generation (full circles) indicate that all four investigated fly ash samples show a similar immersion freezing behavior. However, when particles are being generated from a suspension (open circles) there is a significant decrease in ice nucleation efficiency in comparison to dry particle generation. For droplets containing suspension particles from samples 2, 3, and 4, we could detect nucleation only at temperatures below -35 °C and to a similar extent as for highly diluted ammonium sulphate droplets (gray open circles), indicating that homogeneous nucleation is the dominating ice formation process. The only exception to this observation are wet generated particles from fly ash 1 which retain their ice nucleation ability above -35 °C. Furthermore, we found differences in curve shape in comparison to dry generated particles from the same sample. To investigate possible reasons for the change in immersion freezing behavior dependent on the sample and the particle generation technique, the particles’ composition was investigated by single particle aerosol mass spectrometry. Furthermore, particles were impacted on boron substrates for environmental scanning electron microscopy analysis.

Figure 2. Ice fraction $f_{\text{ice}}$ as a function of temperature $T$ from LACIS measurements with fly ash particles from wet and dry particle generation. Measurements with highly diluted ammonium sulphate droplets are included to indicate the homogeneous freezing range.

Fig. 3 shows $n_s$ values corresponding to the LACIS measurements with wet generated particles, as well as $n_s$ determined from LINA measurements. Here, the values for the four samples vary in a range of two orders of magnitude. Due to the larger amount of material in the droplets (0.1 wt% fly ash in MilliQ water), freezing starts at temperatures between roughly -10 °C and -15 °C and, in most cases, there is no temperature overlap to the LACIS measurements. However, for fly ash 1, where there is a small temperature overlap, there are several orders of magnitude between $n_s$ from LINA measurements and $n_s$ from LACIS measurements. Hypotheses concerning the reasons for this discrepancy include aggregation of particles in the suspension, dissolution of soluble material, or particle size dependent composition/ice nucleation efficiency in the samples.

From our point of view, the effect of methodology on immersion freezing measurements is a highly important one which needs to be considered when quantifying the ice nucleation behavior of certain materials, when sampling atmospheric INP, and in connection with the topic of INP aging.
Figure 3. Comparison of ice nucleation surface site densities \( n_s \) as a function of \( T \) derived from measurements with LACIS and LINA.

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REFERENCES


HETEROGENEOUS NUCLEATION OF SUPERCOOLED WATER NANO-DROPLET AND DROPLET CONTAINING NANOPARTICLES ON ROUGH AND SMOOTH SURFACES: A MOLECULAR DYNAMICS INVESTIGATION

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Keywords: HETEROGENEOUS NUCLEATION, MOLECULAR DYNAMICS SIMULATION, WATER NANO-DROPLET AND NANOFLUIDS, NANOSTRUCTURED SURFACES.

INTRODUCTION

Ice Nucleation in supercooled water is important to an incredibly wide range of everyday as well as global phenomena like the initiation of frost on plants and climate change (Tabazadeh et al., 2002; Murray et al., 2012) to technological processes (Lintunen et al., 2013). Since almost all heterogeneous nucleation process occurs in the presence of foreign particles or solid surfaces (Murray et al., 2012), understanding the relevance between nucleation processes and the structure at the solid-liquid interfaces is a key to study the heterogeneous nucleation. Recent studies report that surfaces with nanometer-scale roughness display freezing delay or suppress ice formation (Meuler et al., 2010; Eberle et al., 2014). In this regard, the understanding at the nanometer-scale roughness where water interacts with surfaces has become an important progressing research area of investigation.

Another great interest in the crystallization process is the role played by nanometer sized particles, suspended in liquid (also known as nanofluids). Nanofluids are important due to its rapidly growing demand in numerous scientific and technological processes. This includes areas such as heat transfer, nanoparticle self-assembly, medical applications and environmental chemistry, to name a few (Das et al., 2006; Zhang et al., 2007; Trisaksri and Wongwises, 2007; Han et al., 2007). The use of suspended nanoparticles (NPs) as the additive to the base liquid can significantly modifying the thermophysical and transport properties such as thermal conductivity, boiling heat transfer coefficient, thermal diffusivity, and viscosity (Trisaksri and Wongwises, 2007; Ahn and Kim, 2012). The wetting as well as nucleation behaviour of nanofluids on the solid surfaces are of particular interest to various technological applications such as microfluidics and nanofluidics processes (Bonn et al., 2009), where surface tension of the nanofluids and the contact area between the solid surfaces and the nanofluids play a vital role to the crystallization processes. In that context, all these phenomena are characterised by the nanometer scale of interfaces where competitive NP-NP, fluid-fluid, NP-surface and NP-fluid interactions have become an important research topic of investigation.

However, accurate capture of nucleation events as well as quantification of the freezing process are difficult due to practical challenges in designing relevant experiments. Therefore, the origin and the underlying mechanisms of heterogeneous nucleation of water remains poorly understood. In that regards, molecular level investigations with direct computational simulations (Auer and Frenkel, 2003) play an important role in the study of nucleation processes. Indeed, the homogeneous nucleation of bulk water has been extensively studied by several research groups using molecular dynamics (MD) and Monte Carlo (MC) simulations. However, relatively few works have been reported on the ice nucleation behavior of supercooled water droplets on smooth and rough surfaces.
In the present study, we use MD simulation to explore the effect of surface roughness and wetting states on ice crystallization of supercooled nano-droplet on the nanostructured surfaces. In addition, we also study the nucleation behaviour of supercooled nanofluid droplet on a smooth surface. Herein we evaluate the nucleation rate and explore the mechanism to inhibit ice nucleation with increasing the nanoparticle concentration in the base fluid.

MODEL AND SIMULATION DETAILS

The textured surfaces are designed using two atomic layers of graphene (AB stacking) as the base layer. An artificial pillar made out of additional graphite sheets is used on top of the base layer. The width and gap between two pillars are varied in both x and y directions to create different roughness. The NPs are modeled as a face center cube (FCC) crystal of 0.408 nm lattice constant, consisting of 43 atoms. A typical water droplet used in this work has 2000 water molecules as the base liquid in a cylindrical shape with a length of 3.4 nm. Figure 1 shows the representative snapshots of a pure liquid and nanofluid droplets placed on a textured and smooth surface, respectively.

Figure 1: Representative cylindrical nanodroplet both from top view (left) and side view (right) of the simulation systems: (A) water droplet on a textured surface and (B) water droplet containing nanoparticle on a smooth surface.

A coarse-grained monatomic model of water, the mW model (Molinero and Moore, 2009) is used. Other cross interactions between substrate-water, substrate-NP and NP-NP are modeled by the two-body term of the Stillinger-Weber (SW) potential. The NP-NP interaction, which occurs between atom-atom is modeled by gold like interaction (Ghorai and Glotzer, 2007). We also study the effect of water-NP interactions by varying the interaction parameter.

In the present study, we used the CHILL algorithm (Moore et al., 2010) to identify ice-like molecule from supercooled water. In order to evaluate the nucleation rate ($J$) of supercooled water, we adopt the mean first-passage time (MFPT) method (Wedekind et al., 2007) in our study. All simulations are performed using LAMMPS simulation package (Plimpton, 2009) under canonical ensemble.

CONCLUSIONS

We investigated the nucleation of a supercooled cylindrical water droplet on nanotextured surfaces at 203 K for the Cassie-Baxter and Wenzel states (as shown in Figure 2A) using molecular dynamics simulations. Figure 2B represents the nucleation rate as a function of surface fraction.

The simulation results show that nucleation rate depends on surface fraction as well as wetting states. The nucleation rate enhances with increasing surface fraction for water in the Cassie-Baxter
state, while contrary behavior is observed for the case of Wenzel state. The estimated nucleation rate indicates that nanostructured surfaces inhibit ice nucleation. The ice-surface work of adhesion for Wenzel states is found to be 1-2 times higher than that in Cassie-Baxter states.

Next, we have studied the nucleation behaviour of supercooled cylindrical nanofluid droplet on a model graphite surface (smooth) at temperature of 215 K. Here the aim of this study is to investigate the effect of nanoparticles concentration in the nanofluids, the NP-water interactions and shape of the NP on the crystallization process. We found that the addition of nanoparticles inhibits rather than enhances the rate of the nucleation of nanoscale droplet during the crystallization process. This behaviour found to be indifferences to water-NP interaction strength; however we observed an optimal interaction strength for ice nucleation in presence of NPs. Further we have examined the shape of the NP on ice crystallization. We found that ice nucleation rate in the presence of cuboid shape NPs is slightly higher compare to spherical shape NPs. Thus, we expect that control over ice nucleation might be achieved by varying the NP concentrations, water-NP interaction, and shape of the nanoparticles. Further, we believe the present work can serve as a platform for processes related to crystallization, condensation and freezing of water in the presence of natural or model aerosol particles.

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REFERENCES


Field and laboratory measurements using continuous flow diffusion chambers (CFDCs) have been used to understand the atmospheric abundance of ice nucleating particles (INPs) and to, in turn, construct parameterizations for mixed-phase and completely glaciated clouds in weather and climate models. This study investigates the measurement of INP concentration and sizing of crystals using CFDCs. We show here that assumptions of ideal instrument behavior are not supported by measurements made with a commercially available CFDC, the SPectrometer for Ice Nucleation (SPIN), and the instrument on which it is based, the Zurich Ice Nucleation Chamber (ZINC). Non-ideal instrument behavior, which is likely inherent to varying degrees in all CFDCs, is caused by exposure of particles to different humidities and/or temperatures than predicted from theory. This can result in a systematic, and variable, underestimation of reported INP concentrations. We further investigate the effects of undercounting INP concentration on simulated cloud forcing in a global climate model. We assess the influence of measurement variability by constructing a stochastic parameterization framework of measurement uncertainty. We find that simulated long wave ice-bearing cloud forcing in a global climate model can vary up to 0.8 W/m² and can change sign from positive to negative within the experimentally constrained bias range. The model results also show significantly different cloud forcing if the bias is considered to be constant, as has previously been assumed, or variable, as suggested by recent experiments. We suggest that detailed measurement, on an instrument-by-instrument basis, be performed to characterize this uncertainty.
SESSION 12:

SUB 10 nm AEROSOL INSTRUMENTATION

Jingkun Jiang: A miniature cylindrical differential mobility analyzer for sub-3 nm particle sizing

Gerhard Steiner: An axial mobility classifier for the size segregation of atmospheric cluster ions

Joonas Vanhanen: Characterization of Dekati Diluter in the 1-20 nm range

Michel Attoui: Characterization of the boosted 3776 butanol TSI CPC as detector in the sub 2 nm range

Florian Dahlkötter: Investigation of particle nucleation events by highly resolved SMPS measurements

Joonas Enroth: On measuring the response time of condensation particle counters
A MINIATURE CYLINDRICAL DIFFERENTIAL MOBILITY ANALYZER FOR SUB-3 NM PARTICLE SIZING

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Keywords: CYLINDRICAL DIFFERENTIAL MOBILITY ANALYZER (DMA); SUB-3 NANOMETER PARTICLES; TRANSFER FUNCTION; NEW PARTICLE FORMATION; SOOT PARTICLE

INTRODUCTION

Understanding aerosol nucleation mechanisms calls for the measurement of sub-3 nm particles. The penetration efficiency and the resolution of a DMA (differential mobility analyzer) for sub-3 nm particles are expected to deteriorate because of the high diffusivity of these particles. The performance of the DEG-SMPS (diethylene glycol- scanning mobility particle spectrometer) can be further improved by having a DMA with better performance when sizing sub-3 nm particles (Jiang et al., 2011b). A DMA designed to size sub-3 nm particles at a moderate sheath flow rate (i.e., 20–30 liters per minute, lpm) will better fit into the DEG-SMPS while keeping its overall package compact and consuming less energy for field studies. Several DMAs for sizing particles in the 1-3 nm size range have been developed. The high-resolution DMAs developed by Fernández de la Mora’s group and the UDMA are designed to operate at high sheath flowrate (typically several hundreds to thousands lpm) rather than matching the flowrate required by the DEG-UCPC. The nano radial DMA (nano-RDMA), whose recommended sheath flow rate is 6 lpm, is a low-flow DMA. Penetration efficiency of the radical opposed migration ion and aerosol classifier (ROMIAC) has not been reported. The cylindrical nanoDMA (TSI Incorporation, Model 3085) was calibrated and temporarily used for sub-3 nm aerosol sizing. However, its sizing resolution for sub-3 nm particles are relatively poor, i.e., 3.90 at the aerosol-to-sheath flow ratio of 2/20 lpm when classifying 1.47 nm particles.

The objective of this study was to develop a miniature cylindrical DMA (mini- cyDMA) with a moderate sheath flow rate to size particles in the 1-3 nm size range. Its transfer function and penetration efficiencies were calibrated using ions of 1.16, 1.47, and 1.70 nm. Finally, the mini- cyDMA was deployed to measure newly formed particles in the atmosphere and nascent soot particles formed in flames.

CONSTRUCTION OF THE MINI- CYDMA

The design of the miniature cyDMA stemmed from the cost-effective DMA (cDMA) developed by Mei et al. (2011). Figure 1 shows all the modifications made to the original cDMA in order to make it operate at 20-30 lpm sheath flow rate. Instead of injecting polydisperse aerosol from two opposite positioned inlet tubes in the cDMA, polydisperse aerosol in the mini- cyDMA is tangentially injected into the polydisperse aerosol chamber for rapid flow distribution. The polydisperse aerosol chamber in the mini- cyDMA was enlarged to dump out the potential tangential flow direction prior to entering the sizing region of the mini-cyDMA. The circular slit for entering the DMA sizing region was also reduced to ensure polydisperse aerosol evenly distributed in the polydisperse aerosol chamber. Classified aerosol is extracted from the classified aerosol flow channel located in the inner cylinder. To enable the higher sheath flow rate operation of the mini- cyDMA (compared with that of the cDMA), the simple cylindrical sheath flow channel used in the cDMA was replaced with a 15° trumpet-shaped flow channel followed by a 45° tapered funnel-shaped channel in the mini- cyDMA. Three layers of 305 nylon screens were installed in
the funnel-shaped channel to keep the flow laminar after passing them. The excess flow chamber was also enlarged to ensure an even distribution of excess flow prior to exiting the mini-cyDMA.

EXPERIMENTAL SETUP AND DATA INVERSION

Standard molecular ions with electrical mobility diameters of 1.16 nm, 1.47 nm, 1.70 nm respectively, were generated to calibrate the transfer functions of the mini-cyDMA (Ude & Fernández de la Mora, 2005). A high resolution short-thin type half-mini DMA (Fernández de la Mora & Kozlowski, 2013) was used to select monodisperse ions. Two Faraday cage electrometers (FCEs) were used as particle concentration detectors upstream and downstream of the mini-cyDMA, and raw counts of the two FCEs were linearly correlated before and after each measurement. When calibrating the mini-cyDMA, the voltage of the half-mini DMA was fixed while the voltage of the mini-cyDMA was increased linearly. A data inversion routine based on empirical diffusive transfer function was used to obtain the transfer functions of the mini-cyDMA, and the detail on this data inversion method can be found in Jiang et al. (2011b). The penetration efficiency, \( \eta_{pen} \), is defined as the efficiency that particles can get through the entrance and exit slits of DMA sizing region, and \( \Omega \) is the DMA diffusional transfer function written as Eq. 2 (Stolzenburg & McMurry, 2008). A parameter to quantify the effect of transfer function broadening is sizing resolution, defined as Eq. 3. An effective diffusion length, \( L_{eff} \), was used to calculate \( \eta_{pen} \) by assuming that particle loss in a DMA can be simulated as diffusion loss in a tube (Karlsson & Martinsson, 2003).

![Diagram](image)

**Figure 1.** (a) Schematic diagram of the miniature cylindrical differential mobility analyzer. (b) Schematic diagram of the calibration system.

\[
\frac{N_2}{N_1} = \eta_{\text{pen}}(d_i) \Omega \left[ Z(d_i), Z'(V) \right]
\]

\[
\Omega = \frac{\sigma}{\sqrt{2\beta(1-\delta)}} \left[ \frac{\tilde{Z}-(1+\beta)}{\sqrt{2\sigma}} + \frac{\tilde{Z}-(1+\beta\delta)}{\sqrt{2\sigma}} - \frac{\tilde{Z}-(1-\beta)}{\sqrt{2\sigma}} - \frac{\tilde{Z}-(1-\beta\delta)}{\sqrt{2\sigma}} \right]
\]

\[
R = Z' / \Delta Z
\]

RESULTS AND DISCUSSION

As the sheath flowrate was increased from 10 lpm to 25 lpm (while keeping the constant aerosol-to-sheath flow ratio of 0.1), the sizing resolution of the mini-cyDMA was improved. At the sheath flowrate of 30 lpm, the sizing resolution decreased to 4.75 (from 5.70 at the sheath flowrate of 25 lpm). \( \eta_{\text{pen}} \) gradually increased with an increase in the sheath flowrate, while appeared to be nearly stable when the sheath flowrate was between 15 lpm and 25 lpm. Thus, the working sheath flowrate of the mini-cyDMA is recommended to be the range of 10 to 25 lpm.
Figure 2(a) illustrates measured penetration efficiencies of the mini-cyDMA versus calculated ones. For both the cDMA and the mini-cyDMA, we found that it is not feasible to find a single effective length to estimate particle loss for various flow rates and various particle sizes. Nonetheless, $L_{eff}$ value can be provided for given flow rates and particles in a certain size range. Figure 2(b) illustrates the comparison of the mini-cyDMA with the Caltech nano-RDMA and the TSI nanoDMA when classifying 1.47 nm ions. The recommended aerosol and sheath flow rates of the Caltech nano-RDMA is 0.6 and 6 lpm, respectively (with $f_s$ smaller than 1.1). Its penetration efficiency and sizing resolution can be further improved by operating it at higher flow rates of 1 and 10 lpm, though deviation from the ideal transfer function occurs at this conditions. Compared to the TSI nanoDMA, the mini-cyDMA has better penetration efficiency and sizing resolution, and is capable of operating at higher flowrate. The mini-cyDMA has similar penetration efficiency and sizing resolution to the Caltech nano-RDMA at 1/10 lpm.

Figure 2. (a) Measured and calculated penetration efficiencies with the effective diffusion length, $L_{eff}$, of 1.50 m and 1.81 m at sheath flow rate of 20 lpm and 25 lpm, respectively. (b) Measured transfer functions of the mini-cyDMA, the TSI nanoDMA, and the Caltech nano-RDMA when classifying 1.47 nm particles.

APPLICATIONS

The DEG-SMPS equipped with the mini-cyDMA was deployed to measure particles in the size range of 1-5 nm in a field campaign in Beijing from March 7th to April 7th, 2016. A PSD (particle size distribution) system (including a SMPS with a TSI nanoDMA, a SMPS with a TSI long DMA, and an APS) was also applied in parallel with the DEG-SMPS to measure particles larger than 3 nm (Liu et al., 2016). The TSI nanoDMA was used for sizing particles in 3-55 nm sizes. A typical new particle formation event occurred on March 13th, 2016, is shown in Figure 43(a). Particle size distributions measured by the DEG-SMPS and the PSD was in good agreement, e.g., the coefficient of determination, $R^2$, of particle size distribution of 4.7 nm particles measured by both instruments was $0.97$. The mini-cyDMA was also applied in the laboratory soot studies. Details about the burner and the sampling systems can be found elsewhere (Tang et al., 2017). The DEG-SMPS equipped with the mini-cyDMA and the PSD were used in parallel to measure soot particles. A typical soot particle size distribution measured at a burner-to-stagnation surface separation distance of 0.6 cm and at the fuel-to-oxygen stoichiometric ratio of 2.0 is shown in Figure 3(b). Size distributions by the DEG-SMPS agree well with those by the PSD. The average relative error between two set of data in 3-5 nm size range is $2.3\%$.

CONCLUSIONS

A mini-cyDMA was developed for effective classification of particles in 1-3 nm size range. 305 mesh nylon screens (in three layers) were used to keep the DMA sheath flow laminar. Instead of two opposite-positioned inlet tubes, polydisperse aerosol is tangentially transported into the polydisperse aerosol chamber in the mini-cyDMA. The flow chambers for polydisperse aerosol and excess flow were enlarged to enable higher flowrate operation than the cDMA. Transfer functions and penetration efficiencies of the
mini-cyDMA classifying 1.16 nm, 1.47 nm, and 1.70 nm standard ions, respectively, with the sheath flow rate range of 10-30 lpm were measured. A data analysis routine based on the diffusional transfer function and the penetration efficiency was used. Effective diffusion lengths of the mini-cyDMA were estimated to be 1.50 m and 1.81 m, respectively, when the aerosol-to-sheath flow rates are 2/20 lpm and 2.5/25 lpm. Compared to the TSI nanoDMA, the mini-cyDMA has better penetration efficiency and sizing resolution. The mini-cyDMA was incorporated into a prototype DEG-SMPS to characterize new particle formation events in the atmosphere and to measure nascent soot particles generated by a premixed flame. In the overlapping size range of 3-5 nm, good agreements were observed between the DEG-SMPS using the mini-cyDMA and the PSD using a TSI nanoDMA.

Figure 3. (a) A typical atmospheric new particle formation event observed in Beijing and (b) size distributions of nascent soot particles measured by the PSD and the DEG-SMPS equipped with the mini-cyDMA.

ACKNOWLEDGEMENTS

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REFERENCES


AN AXIAL MOBILITY CLASSIFIER FOR THE SIZE SEGREGATION OF ATMOSPHERIC CLUSTER IONS

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INTRODUCTION

In the last years, huge efforts have been made to gain deeper insights in the detailed mechanisms of atmospheric new particle formation (e.g. Bianchi et al. 2016; Kirkby et al. 2016; Tröstl et al. 2016). The key instruments for this undertaking have demonstrated to be new types of Atmospheric Pressure interface-Time of Flight (API-TOF) mass spectrometers (MS) (e.g. Junninen et al., 2010). Still, it remains an open question, whether the contributing mechanisms are correctly depicted by the presently used instrumentation or if only strongly bonded core clusters without loosely bonded ligands have been detected so far. Therefore, we have developed a new type of inlet for a high resolution TOF-MS, aimed to investigate fragmentation and evaporation processes of loosely bonded ligands from ionic molecular clusters in the sub 2nm size range – the so called “nanoTOF”. One of the main features of the new inlet is the so called Axial Mobility Classifier (AMC), only allowing ions with a specific ion mobility to enter the instrument for further detection. This way, together with an also integrated Collision Induced Dissociation Cell (CID cell), the AMC allows the monitoring of the degree of fragmentation of the ion clusters in the CID cell.

METHODS

The working principle of the AMC uses a similar approach as recently presented by Bezantakos et al. (2015) and Tammet (2015): an electric field, opposed to the instrument’s inlet flow, is slowing down the ions and only allows ions below a certain critical electrical mobility to pass the potential maximum. By continuously reducing the potential barrier, also ions with higher mobilities are allowed to pass; illustrated in figure 1 for positively charged clusters.

Figure 1: Working principle of the axial mobility classifier for positively charged clusters
EXPERIMENTAL

The experimental setup for testing the ion transmission efficiency and the mobility classification characteristics of the nanoTOF inlet with the integrated AMC is schematically shown in figure 2.

![Schematics setup](image)

Figure 2: Schematics setup for the characterization and performance testing of the nanoTOF inlet with integrated Axial Mobility Classifier (AMC).

The core part of this setup is the so called Cluster Calibration Unit (CCU), consisting of a Vienna-type high resolution Differential Mobility Analyzer (UDMA, Steiner et al. 2010) for size segregation, and a custom-built electrospray ion source for the generation of well-defined monomobile molecular clusters. Two aerosol electrometers (EM1 and EM2) upstream and downstream of the nanoTOF inlet allow the determination of the mobility/mass dependent overall ion transmission efficiency and the mobility classification of the AMC. A set of AMC mobility scans of electrospray generated tetra-alkyl ammonium halide clusters is shown in Figure 3.

![Mobility scans](image)

Figure 3: Mobility scans of electrospray generated tetra-alkyl ammonium halide clusters with the Axial Mobility Classifier (AMC)
Five individual AMC mobility scans with each cluster species having a different ion mobility are shown. By scanning the AMC voltage (for example) from high voltage to low voltage, for a given cluster the transmission efficiency over the potential barrier is incrementally increased. Below a certain voltage, all clusters are allowed to pass. The slope of the resulting penetration efficiency curve determines the resolution power of the AMC with respect to the electrical mobility. The comparison of the final plateau value of the electrometer signal detected by EM2 downstream of the inlet and the ion signal reading from EM 1 upstream, enables the determination of the total mobility/size/mass dependent ion transmission efficiency of the nanoTOF inlet.

Similar experiments, based on computational fluid dynamic (CFD) simulations of ion trajectories in the AMC inlet were performed using the open-source CFD software distribution OpenFOAM. The CFD simulations provide a more sophisticated tool to study the transmission properties of charged particles of different electrical mobility or mobility diameters respectively (figure 4).

CONCLUSIONS

For typical operating conditions of the new nanoTOF inlet with the integrated AMC, an ion transmission efficiency between 40-50% was found for all studied tetra alkyl ammonium halide clusters. The resolution power of the AMC with respect to the electrical mobility, as defined by Flagan (1999), was determined to be in the range of R=3-4 for the studied clusters in the current configuration of the inlet. Further optimization of the inlet is scheduled for an improved mobility classification performance.

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REFERENCES


Characterization of Dekati Diluter in the 1-20 nm particle size range

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Keywords: dilution, cluster, particle number.

INTRODUCTION

One of the main advantages of condensation particle counters is the sensitivity (McMurry, 2000). The ability to detect individual particles is crucial in many applications. A CPC can be used as single particle detector usually up to about $10^4 \text{#/cm}^3$, after which coincidence starts to be an issue (>10% of the signal). For higher number concentrations CPCs can use so called cloud mode, or some method of dilution can be applied. The cloud mode is based on correcting measured signal with a parametrization determined through calibration of the individual instrument against a known particle number concentration. In the cloud mode, the instrument loses its ability to detect single particles. Using dilution allows one to measure with single particle detection mode and hence get more precise measurements. For the smallest aerosol particles and clusters of molecules, dilution is not trivial due to diffusional losses to the walls of the diluter. In the recent years CPC technology, and also the calibration methods have been developed and the lowest cut-off diameters are now pushed to the sub 2 nm size range (Vanhanen et al. 2011, Jiang et al. 2011, Kangasluoma et al. 2015). This creates a need for a diluter design suitable also for these smallest clusters. In this study, we characterized the Dekati ejector diluter (Dekati Diluter), in the particle size range of 1-20 nm in diameter. The hypothesis to be verified was that the high volumetric flow rates used in the Dekati ejector diluter should reduce the diffusional losses of the smallest aerosol particles.

METHODS

Two different measurement setups were used in this study; a Hauke DMA – setup and a high flow DMA – setup. With the Hauke DMA a tube furnace with nitrogen as carrier gas was used to produce silver nanoparticles and an Americium neutralizer was used to achieve the charge equilibrium before the DMA. The particle diameter size range measured with this setup was from 4.1 to 20 nm. Both the CPC after the diluter and the reference CPC have 50% cut-off diameters at 6 nm. The CPC cut-off curves were taken into account within the whole size range when analyzing the data.

Figure 1. Hauke DMA setup.
With the high flow DMA (SEADM, HalfMini) a hot wire generator with NiCr – wire and HEPA filtered compressed air as a carrier gas was used to produce nanoparticles. The hot wire generator produces so called self-charged particles and thus no additional neutralizer / charger was used (Kangaslouma et al. 2013). An aerosol electrometer was used as a reference instrument and Airmodus A11 nano Condensation Nucleus Counter (nCNC) was used as the detector after Dekati Diluter. The nCNC was calibrated carefully against the electrometer before the measurements and the high flow DMA was calibrated by using known mobility standards (Ude and de la Mora, 2005).

![Diagram of high flow DMA setup]

**Figure 2. High flow DMA setup.**

The dilution factor of the Dekati ejector diluter is calibrated by the manufacturer by measuring the inlet flow rate and the pressure difference of the inlet and the outlet of the diluter. With zero pressure difference the dilution factor is 7.96. Measured pressure difference between the inlet of the ejector and the outlet of the ejector was about 20 mbars and the dilution factor without particle losses according to the data sheet should be about 9. This dilution factor doesn’t take into account the particle losses inside the diluter. For small particles, the main particle loss mechanism is diffusion to the walls of the diluter. By comparing the concentrations of a reference instrument and the instrument after the Dekati Diluter, so called particle number concentration reduction factor (PCRF) can be calculated. This factor contains both the dilution and the particle losses inside the diluter.

In figure 3, the particle number concentration reduction factor (PCRF) and the estimated particle losses are presented as a function of the particle diameter. The PCRF above 10 nm is relatively constant with mean value of 9.31. This is well in line with the factory calibration using only flow measurements, giving a dilution factor of about 9 with the pressure difference measured in this study. The PCRF increases towards the smallest particle size measured in this study (44.4 at 1.2 nm). We assume that this is due to diffusional losses inside the diluter. If the dilution factor of 9.31 is taken into account, the particle losses for 1.2 nm particles inside the Dekati Diluter are 79%. This is still quite reasonable when considering the high diffusivity of such small clusters. Already at 1.9 nm the losses are 43%. 
CONCLUSIONS

The Dekati ejector diluter was tested using two different measurement setups in the 1-20 nm particle size range. The particle number concentration reduction factor (PCRF) was measured and the particle loss factors for different sizes were calculated. The dilution factor was found to be constant above 10 nm and the particle losses were significant only below 3 nm. For the smallest particle size of 1.2 nm the losses were about 79%, but already at 1.9 nm the losses were below 50%. Based on the results the Dekati Diluter can well be combined with Airmodus nCNC, provided the particle number concentration reduction factor as a function of particle size is included in data inversion.

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REFERENCES

Characterization of the boosted 3776 butanol TSI CPC as detector in the sub 2 nm range.
Activation of sub 2 nm with butanol vapors.

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Boosted butanol laminar sheathed condensers CPCs have (Kuang2012) demonstrated their ability to detect sub 3 nm with acceptable detection efficiency although lower than mixing cpc with di ethylene glycol as working fluid. In the other hand Kangastuoma et al. 2015 have showed than unsheathed condensers butanol CPCs are able to detect particles down to 1 nm. So if unsheathed condenser can detect particles of 1 nm why not the sheathed condenser CPC design?

The new TSI 3776 butanol CPC which is the successor of the well-known ultrafine 3025 based on the work of Mark Stolzenburg and Peter McMurry (in AS&T) is used in this study to explore the capabilities of butanol to activate sub 2 nm at the limit of the homogeneous nucleation.

To increase the detection efficiency of any CPC or growth system one has to fight against the diffusion losses of particles in the transport and sampling lines until the inlet of the condenser in one hand. The second task is to increase the activation probability versus the size of the particles. Both problems are related to the sub 5 nm aerosol particles of course. The problem is even worst when the particles are smaller than 2 nm.

The design of the ultrafine TSI CPCs (3025&3776 models) are used successfully since more than 25 years to detect with 50% detection efficiency particles larger 3 nm. The flowrate in the activation area (or condenser) also called detected flow rate because it’s the flowrate which crosses the optical detector was and still fixed at 0.3 lpm since the introduction of laminar CPCs by TSI in the early 80s (model 3020).

In the ultrafine design a part of this detected flowrate is used to sheath the introduced aerosol particles along the axis of the condenser. The sheath air has two main goals: keep the particles far from the condenser walls to reduce their diffusion losses and give them more opportunity to be activated and grow by exposing them to the maximum supersaturation profile which is the long of the condenser axis (Stolzenburg thesis).

\[ Q_{\text{total}} = Q_{\text{sheath}} + Q_{\text{aerosol}} = 0.3 \text{ lpm} \]

Figure 1
Design of the sheathed condenser of the ultrafine CPC.

The particles emerge along the axis of the condenser from the saturator through a short capillary tube (ID and Length) with a small flowrate (one tenth of the condenser flow in the work of Mark Stolzenburg and the 3015 TSI CPC). The losses inside the capillary start to be consequent for particles smaller than 5 nm because of this low flow (0.03 lpm). The transport flow of particles is kept high enough (1.5lpm) until the inlet of the capillary tube which makes the losses negligible.

There are different parameters to play with if one is concerned by an augmentation of the DE of this design.

1°) Increase the supersaturation until the limit where the homogenous nucleation start to produce droplets with high rate (> 1 particle per second) by increasing the temperature difference between the saturator and the condenser of the CPC at constant condenser flowrate (0.3lpm).
2° Increase the flowrate in the capillary to reduce the losses. This leads to a consequence of reducing the sheath flow of course in the condenser. In the other hand it reduces the amount of vapor molecules of butanol arriving in the condenser since the sheath flowrate will decrease.

3° Increase the flowrate in the condenser to decrease the diffusion losses of the particles. This is not accessible nor unintended in our study with the commercial version of the ultrafine 3776 CPC.

As we can see the reduction of the sheath flow around the capillary can have positive and negative sides as always. The positive point is that the losses inside the capillary are reduced. In the other hand the highest temperature difference (ΔT) between the condenser and the saturator which gives to lower rate of homogeneous nucleation is higher.

The negative points are the reduction of the amount of vapor in the condenser and the decrease of the confinement efficiency of the particles in the middle of the condenser during their growth time before the optical detector. A low sheath flowrate can also have another consequence. The molecule of butanol will have ‘opportunity’ to diffuse to the cold wall which makes them lost or ‘vacant’ for the growth of the particles.

The conclusion of this short discussion is that one have to find the right balance in the case of the commercial instrument used in this study. For the next work and or project it would be a very good idea to add the length of the condenser and the detected flowrate in the growth tube as a key parameters in our research objectives.

Two different flowrate are tested in this study: 50 and 70 cc per minute. The total flowrate in the condenser id kept constant and equal to 0.3 lpm (300 cc/min). The temperature of the condenser is kept constant and equal to 10°C. The temperature of the saturators varies from 39 to 48°C for 10 cc/min in the capillary and 39 to 45°C for 50cc/min.

Indeed the limit or threshold of the homogenous nucleation is not the same for both aerosol flowrates in the capillary. The homogeneous nucleation is a function of the butanol vapor number concentration (molecules /cc) coming from the saturation. This concentration in turn is proportional to the sheath air flowrate coming from the saturator. The homogenous limit for 10 cc/min aerosol flow in the capillary is given by a ΔT between the saturator and the condensor 10/48 °C. For 50 cc/min the ΔT is 10/45°C. Let us note once again that the total flowrate in the condenser is kept constant and equal to 0.3 lpm (300cc/min).

The experimental set up used in the study is the classical set up where we have a high resolution and high flow DMA (Attoi type) a home-made high flow electrospray source a TSI 3776 butanol CPC a Fraday Cage connected to a Kerithley electrometer (model 6517)

THABr (tetraheptylammonium bromide, TBABr (Tetrabutylammonium bromide) and NiCr oxides are used as particle tests in positive and in negative mode. TBABr is hygroscopic and highly soluble in water (600g/l). THABr is hydrophobic and non water soluble.

Results and discussion.

The goal of the study is not to enhance the detection efficiency of the CPC. The goal is to use the abilities of the CPC in terms of flowrates control (sheath and capillary) to study the activation (or no activation) of THABr and TBABr monomer by lowering the aerosol losses in the capillary and working at the limit or threshold of the homogeneous nucleation.

The presentation gives the effect of the flowrate in the capillary on the detection efficiency for different DTs until the limit of the homogeneous nucleation.

The figures 1 and 2 below give the inverse mobility spectra of TBABr (tetraheptylammonium bromide) with flowrates of 50 cc/min 70 cc/min in the capillary at the limit of the homogeneous nucleation and respectively in the condenser. The figures give the signal intensities measured in parallel with the aerosol electrometer and the CPC.

The figures 3 and 4 give the results with THABr (tetraheptylammonium bromide) in the same with 50 et 70 cc/min aerosol flowrate in the capillary at the limit of the homogeneous nucleation always.
Let us remind that the first peak (monomer) and second (dimer) from the left of THABr are 1.47 and 1.78 nm mobility diameter. The monomer (first peak) and second peak from the left of the TBABr are 1.24 and 1.5 nm mobility diameters.

Figure 1
TBABr with 50 cc/min in the capillary

Figure 2
TBABr with 70 cc/min in the capillary

Figure 3
THABr with 50cc/min in the capillary

Figure 4
THABr with 70 cc/min in the capillary

References:


INVESTIGATION OF PARTICLE NUCLEATION EVENTS BY HIGHLY RESOLVED SMPS MEASUREMENTS


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Keywords: PARTICLE SIZE DISTRIBUTION, NUCLEATION, INSTRUMENTATION, MEASUREMENT

INTRODUCTION

Nucleation and new particle formation (NPF) events can make a significant contribution to particle number concentrations in remote locations (Kulmala and Kerminen, 2008) as well as urban locations (e.g. Brines et al., 2015). While the remote NPF events have been subject to observations for years and are quite well understood, urban NPF still needs further investigations due to the complex chemistry, various precursor species and wide range of pollutants involved. Especially with decreasing particle concentrations due to improved technologies in the main emitting processes, the urban NPF events might increase in frequency (Brines et al., 2015). For both cases, such atmospherically relevant processes are frequently observed and measured with Scanning Mobility Particle Sizer (SMPS) systems. With an SMPS, the number size distribution is measured and nucleation as origin of the new particle formation process is observed and quantified. As NPF start at particles with sizes of a few nanometers (e.g. Dal Maso et al., 2005), the SMPS systems must be capable of measuring particles as small as possible to be able to fully understand and characterize NPF processes. This study presents measurements of NPF events using an advanced model of the well-established SMPS that is capable of measuring particle size distributions in a range starting at 1 nm.

METHODS

Several NPF measurements conducted with SMPS systems just measured the upper part of the particle size distribution due to limitations in the lower cutoff diameter of the systems. The recently released 1 nm-SMPS (Dahlkötter et al., 2016) provides a new high-resolution method for fast measurements of particle size distributions starting at 1 nm (D50 at 1.1 nm geometric diameter or 1.4 nm electrical mobility diameter). This lower cutoff size is achieved by introducing of the Nano Enhancer (TSI Inc., Model 3777) and improving the Differential Mobility Analyzer (DMA) to a 1 nm-DMA (TSI Inc., Model 3086) as new components of the modular SMPS. In the Nano Enhancer the particles are enlarged respectively pre-grown using diethylene glycol (DEG) before entering a butanol-based CPC as detector. This system is based on previous prototypes as described in Lida et al. (2009), Jiang et al. (2011), Wimmer et al. (2013) and Zhao et al. (2015). Table 1 shows the components of the 1 nm SMPS used in this study. The performance of the 1 nm-SMPS was already documented in laboratory experiments (Chandra et al., 2016; Dahlkötter et al., 2016).
<table>
<thead>
<tr>
<th>Component</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic Classifier (EC)</td>
<td>3082</td>
</tr>
<tr>
<td>Neutralizer</td>
<td>3088 or 3077A</td>
</tr>
<tr>
<td>Differential Mobility Analyzer (1nm-DMA)</td>
<td>3086</td>
</tr>
<tr>
<td>Nano Enhancer</td>
<td>3777</td>
</tr>
<tr>
<td>Condensation Particle Counter (CPC)</td>
<td>3772</td>
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</tbody>
</table>

Table 1. Components of the 1 nm SMPS system.

In this study we conducted first measurements of NPF events using this system that revealed a compelling picture of the lower end of the particle size distribution. Chandra et al. (2016) reported on measurements of NPF events with the 1 nm-SMPS on Fukue Island, Japan. Our measurements were done in Madrid as part of a larger measurement campaign, in order to observe NPF events under urban conditions. Figure 1 shows the results of two NPF events we observed. The cutout in that figure underlines the importance of the ability to measure particle size distributions down to the 1 nm-range to understand at what size new particles start to form. The continuation of the nucleation and growth was observed by a long-SMPS at the same station. The lower size range is crucial for the understanding of the complex systems based on the variety of gaseous precursor species, environmental conditions and background particle concentration levels. In our study the sampling setup could not be fully optimized during these measurements due to restrictions in the level of modification of the installation. We therefore had to take into account a significant amount of diffusion losses in the sampling inlet lines, indicating that the presence of even smaller particles than measured is possible and likely. While this optimization potential is regrettable, it does support the importance of the size range from 1 nm to 3 nm during the measurement of NPF events.

Figure 1. Averaged particle number size distribution of two NPF events measured with the 1 nm-SMPS in Madrid (14th July 2016, 06:50 – 09:35, and 15th July 2016, 07:15 – 09:10).
CONCLUSIONS

The data we presented exemplarily show the size distributions of two NPF events observed in July 2016 in Madrid and underline the relevance of nucleation processes for particle concentrations in urban environments. Time-resolved measurements of the smallest particles in this size range, as now possible with the 1 nm-SMPS, will improve the level of understanding of urban NPF processes and contributing environmental conditions. In addition, the measurements and data presented underline that it is highly desirable to optimize the measurement setup to minimize the uncertainties caused by diffusion losses. Apart from urban studies, this advanced model of the SMPS that we used in this short urban study will also be suitable to further understanding of NPF processes in remote locations due to its highly-resolved particle sizing and counting capability in the size range of 1 – 50 nm. We will present the results from the SMPS in Madrid and possible other ambient data that show the lower end of the particle size distribution, relevant to complete and improve the exiting observations of NPFs.

ACKNOWLEDGEMENTS

We thank our partner Alava Ingenieros in particular Enrique Latorre for the local support. CIEMAT participation was through projects PROACLIM (CGL2014- 52877-R) and TECNAIRE (P2013/MAE-2972). CSIC participation was funded by the Spanish Ministry of Environment, the regional government of Madrid and the city council of Madrid.

REFERENCES


Zhao, J., Han, H. S., Karn, A., and P. H. McMurry (2015). Design Refinements for a 1 nm DEG Ultrafine Condensation Particle Counter (UCPC), at 34th AAAR Annual Conference (Minneapolis, MN, USA), Paper number 2.1M.21.
ON MEASURING THE RESPONSE TIME OF CONDENSATION PARTICLE COUNTERS

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Keywords: RESPONSE TIME, PARTICLE COUNTER, SPARK GENERATOR.

INTRODUCTION

Fast particle counting is a desirable attribute for various measurement purposes. Mobile measurements, rapid size scans or flux measurements are some of the applications where ever faster particle counting is desired. These requirements are being answered with the introduction of fast water based condensation particle counters (CPC) by TSI and by introducing alternative designs solutions such as the mixing type CPC’s of Wang et al. (2002) and Wehner et al. (2011).

These fast response instruments require more precise measurement of their their temporal resolution than the traditional laminar flow CPCs. The older models, such as the 3010 by TSI have typically slower (> 1 s) rise times (time taken for concentration to change from 10 to 90 %), while the novel faster CPC’s state to have even sub-100 ms rise times. This acceleration of an order of magnitude makes it important to understand thoroughly the process of determining a CPCs time response, and the numerous factors that take part in shaping, and potentially distorting, the observed response. Some of these factors work to slow the response (diffusion in tubing, slow change in concentration control, size dependent terminal velocities etc.), while others can have the opposite effect (pressure pulses, coincidence).

The accurate understanding of the response time is not only a technical curiosity, but of importance for correct data interpretation. Overestimation of the response time is usually less dangerous, and mostly translates only to poorer measurement resolution, either spatial or temporal. The underestimation, however, is prone to distort measurement data by the residual effect of the previous measurement points, and therefore it is vital to know the true response time of the instrument, provided you want to run your instrumentation near to its maximum temporal resolution.

Various methods have been implemented in determining the response time of CPCs that include valves (Quan et al. 1992; Hering et al. 2005), spark generators (Wang et al., 2002) or DMAs (Buzorius, 2001; Shi et al. 2005). None of the methods has gained universal adaptation even in more recent studies. Here we present results of a comparison of different methods found in the literature for determining a CPC’s time response. All the experiments described here were using a single fast mixing type CPC built in the University of Helsinki as the detector.

Like the methodology, the terminology also has not been fully set. The mixing time depicted as τ, is the most widely adopted common term, which is used to indicate the time constant with respect to a particle concentration change. As the name implies, this is meant to describe the diffusional movement, or mixing, of particles within the instrument. The resulting response to a concentration change is thus well described using a first order exponential function (Eq. 1).

\[ N(t) = N_i + (N_e - N_i) \cdot \exp \left( -\frac{t}{\tau} \right) \]  \hspace{1cm} (1)
Many studies report the response of their respective instruments using the $\tau$. However, from this definition it is not immediately obvious to the end user what is the practical maximum time resolution, and hence here we adopt the use of $\epsilon$ to indicate the response time, defines as

$$\epsilon = 3 \times \tau$$ (2)

$\epsilon$, introduced for the sake of clarity, corresponds to a change in concentration of 95 % (either 0% - 95% or 100 % - 5%). This definition of a response time allows a more useful interpretation of the change, while still being strictly mathematical in its description.

METHODS

We tested different methods found in the literature for the determination of particle counters response time in order to find the most suitable method for producing robust and highly reproducible response times. The most popular methods included using a Differential Mobility Analyzer (DMA), a spark generator or a valve to produce a rapid change in the particle concentration of the sampled air.

Using rapid control of voltage in a DMA Buzorius (2001) determined the response time for a TSI 3010 CPC. Following this approach, we used a short Vienna type DMA, with 4 lpm aerosol flow and 20 lpm sheath flow. Additional particle free carrier air was added right after the DMA to ensure turbulent flow, and hence a plug flow profile.

Another approach has been to use spark generators, for instance Wang et al. (2002) and Shah and Cocker (2004) in studying fast mixing type CPCs. Here, the spark generator was tested using different levels of dilution, which all had Reynolds numbers well more than 4000, again ensuring the turbulent flow profile was maintained until the inlet of the instrument. The spark generator works by applying high voltage to electrodes which then are brought close enough so that a spark discharge occurs (Schwyn et al. 1988). This produces a sharp pulse of particles, which then can be used to determine the response time.

The use of valves has been one of the more popular methods for response time determination used for instance in studies by Quant et al. (1991), Hering et al. (2005), Heim et al. (2004), Held and Klemm (2006). Unlike in these previous studies, here the valve did not sample from ambient air, but was connected to an atomizer and an additional carrier/dilution flow was used to ensure turbulent flow in the tubing. The used set-up is shown in Figure 1.

![Figure 1. CPC response time measurement set-up used for the valve based measurements.](image)

CONCLUSIONS

The results of these various response time measurement methods are illustrated in Fig 2. All data in the figure is from the same fast mixing type CPC, hence the differences should not originate from the instrument, but rather the different test methods.
The DMA method, even with the added carrier flow and the high aerosol and sheath flow rates, proved to be the slowest of the tested methods. It is viable, that using high-flow DMA’s and more advanced power sources, this method can be significantly improved, however the traditional DMA’s appear not to be suited for the task.

The spark method was found to produce varied results. An attribute of the spark generator is to produce very high concentrations that can exceed the coincidence limit of most CPCs (Schwyn et al. 1988). The presence of coincidence was observed to have a significant impact on the measured response time, with higher concentrations having a more drastic impact. Figure 2 shows the concentration decay as determined from either high (> 50 000 # cm$^{-3}$) or low (< 4 000 # cm$^{-3}$) concentration spark. The high concentration spark appears to have a slower response, due to masking effect of coincidence. While the actual concentration decreases quite drastically, the observed concentration shows a less pronounced decay, thus resulting in a slower appearing response. It should be mentioned, that the opposite is true if one looks at the concentration increase. In that case coincidence creates an artificial plateau in the concentration, and makes the instrument appear to be faster than it is. These problems can easily be avoided by applying suitable dilution and voltage settings so as not have concentrations in the coincidence range.

When the spark generator was operated using the low concentrations, the decay response appeared to give more consistent and reasonable results. Unfortunately, the concentration increase could not still be extracted using this method. The peak of the spark pulse is likely to be too transient to be correctly captured, and the final plateau value for the concentration cannot be therefore know. This effectively means that the concentration increase is extremely hard to determine from the spark generator.

In contrast to the spark method, the valve method allows for very fine particle concentration control, especially if connected to a constant aerosol source, like an atomizer. This makes it easy to avoid coincidence, while ensuring sufficient signal given the large dilution flows needed to maintain turbulent condition in the sampling lines. Furthermore, the valve method also allows the determination of the instruments response to a step change for both concentration increase and decrease.

The main problem found with the valve method is the small pressure pulse that is associated with the changing of the valve. This can affect the flows of some the sheathed instruments by distorting the internal flows of the instrument. This however was not found to be a major issue, as shown in Figure 3. Both the spark and valve methods showed considerable agreement, and are likely suitable for the determination of the response time of even the faster particle counters.

Figure 2. Observed responses for various response time measurement set-ups. Concentrations < 4000 # cm$^{-3}$ were used for all measurement but the High conc. spark, where concentrations exceeding 50 000 # cm$^{-3}$ were used. The solid lines indicate the data fitted to Eq. 1.
Figure 3. Normalized concentration decay from spark and valve measurements. The squares depict the median of the spark measurements, with the dotted line a fit according to Eq.1. The filled circles depict the median of the valve measurements, with the solid line showing the corresponding fit.

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REFERENCES

Shi, Q., H. S. Han, S.W. Kerrigan, and E. M. Johnson, Characterization of Two New Butanol-based Condensation Particle Counters, poster #1PC17, American Association for Aerosol Research Conference, Austin, Texas, October 2005.
SESSION 13:
ATMOSPHERIC CHEMISTRY

Chao Yan: The impact of NOx on oxidation products of monoterpenes and the subsequent nano-particle formation

Olga Garmash: The effect of NOx on distribution of highly oxygenated molecules in aromatic systems

Katerina Karadima: Effect of organic content and humidity on the structure of atmospheric nanoparticles: a molecular dynamics study

Anna Hodshire: Nucleation and growth under high OH conditions

Siegfried Schobesberger: Quantifying oligomerization in organic aerosol through desorption thermogram modeling

Alexander Laskin: Atmospheric particles from unrecognized atmosphere-land interactions

Gennady Gor: Kinetic model for condensation-induced restructuring of atmospheric soot agglomerates
THE IMPACT OF NO$_x$ ON OXIDATION PRODUCTS OF MONOTERPENES AND THE SUBSEQUENT NANO-PARTICLE FORMATION AND GROWTH

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Keywords: NO$_x$, HOMs, NANO-PARTICLE FORMATION

INTRODUCTION

Atmospheric aerosol particles have a significant impact on the Earth’s climate (IPCC 2013). One important source of these particles is the formation and subsequent growth of new aerosol particles directly in the atmosphere (secondary aerosol), which potentially has a large contribution to the budget of cloud condensation nuclei (CCN) on a global scale (Merikanto et al., 2009; Dunne et al., 2016).

In the past decade, organic vapors have been recognized as an important source of secondary aerosol mass, through the condensation of their various oxidation products on pre-existing particles (Jimenez et al., 2009). Recent chamber studies have shown that some oxidized products with very low volatility can contribute to the initial growth of newly formed particles (Ehn et al., 2014, Tröstl et al., 2016), and even participate in the nucleation process (Kirkby et al., 2016). Alpha-pinene, a common monoterpenene, was chosen as the VOC (Volatile Organic Compound) precursor in the abovementioned studies, as it is one of the most abundant biogenic VOCs globally, especially in high-latitude regions. After the initiation of oxidation by O$_3$ and/or OH, the intermediate products may undergo fast auto-oxidation until a termination reaction occurs, forming highly oxidized multifunctional compounds (HOMs) (Ehn et al., 2014, Jokinen et al., 2015, Rissanen et al., 2015).

The ubiquitous nitrogen oxides (NO$_x$) in the atmosphere have a significant influence on the VOC oxidation, through reacting with peroxy radicals or initiating the oxidation by NO$_x$, leading to various products, many of which are nitrogen-containing compounds (Hallquist et al., 2009). Even in remote or rural areas, such as the SMEAR II station in southern Finland (Hari and Kulmala, 2005), where the mixing ratios of NO are very low (hourly average NO$_2$ concentration $\approx$ 1 ppb and NO concentration $\approx$ 50 ppt), NO$_x$ still has a strong influence on the HOM production (Yan et al., 2016, Lee et al., 2016). Accurate aerosol modelling requires a better understanding of the extent that NO$_x$ modifies the oxidation pathways, as well as detailed information of the oxidation products.

The ultra-clean CLOUD chamber (Kirkby et al., 2011, Duplissy et al., 2016), which is equipped with state-of-the-art instruments, allows the study of HOM production and aerosol formation under atmospherically relevant levels of NO$_x$. By identifying the HOMs produced under various NO$_x$ conditions,
we deduced their plausible reaction pathways. We further characterized the growth rate of newly formed particles to study the effect of NOx on aerosol particle formation.

METHODS

We studied the effect of NOx on HOM production and aerosol formation in the CERN CLOUD chamber during the CLOUD10 campaign in fall 2015. Two most globally abundant monoterpenes, alpha-pinene and delta-3-carene, were used as the VOC precursors. We varied their total concentration from 300 to 1200 ppt, while keeping their initial ratio constant at 2:1. As sulphuric acid (SA) is known as an important contributor to aerosol formation, to better mimic the atmospheric particle growth, we also added 0.6 - 3.3 ppb of SO2, which produced about 0.5 - 2 ppt SA. We refer to each monoterpane-SA concentration pair as one run. During each run, we injected three levels of NO into the chamber, most of which was quickly converted into NO2 by O3, and a small fraction of NO2 was further oxidized to NO3. The NO (NO+NO2) concentration was measured as 0 – 5.2 ppb with a constant ratio between NO and NO2 (at ca. 0.6%).

We characterized the HOM production and nano-particle formation and growth in this SA-monomonoterpene-NOx 3-dimensional parameter space with various instruments. A time-of-flight chemical ionization mass spectrometer (tof-CIMS, also known as CI-API-TOF) using nitrate as the reagent ion was used to measure the composition and concentration of sulfuric acid as well as highly oxidized products from monoterpenes (Jokinen et al., 2012, Ehn et al., 2014). Another tof-CIMS equipped with a FIGAERO sampling inlet, using iodide (I) as the reagent ion, was used to measure the chemical composition of the aerosol particles and the desorption temperature of these compounds. In addition, we deployed a set of instruments to measure size-segregated particle formation and growth, including a PSM (particle size magnifier, Vanhanen et al. 2011), a DMA-Train (Stolzenburg et al. 2016), a NAIS (Mirme and Mirme, 2013), and a TSI nano-SMPS.

CONCLUSIONS

Figure 1 exhibits a typical run sequence when the concentration of NO was increased stepwise into the chamber. The time evolution of some example HOMs is shown in the bottom panel, each of which instantaneously responded to the NOx changes in different ways, suggesting multiple reaction pathways were influenced or created by NOx. Such changes in HOMs had pronounced influence on aerosol formation. As shown in the top panel, the aerosol formation was significantly suppressed when adding NOx.
Figure 1. Temporal evolution of representative HOMs (bottom panel) and particle size distribution (top panel) when various levels of NO₃ (middle panel) and ion concentrations (not shown) were present in the chamber.

We will present more detailed information on the identities of various NO₃-relevant oxidation products and their plausible formation pathways that are deduced based on their elemental compositions as well as their responses to NO₃ variation. We will show to what extent the chemical processes observed in our chamber study can be found in the atmosphere. By characterizing the properties of such NO₃-relevant products, we will attempt to explain the negative effect of NO₃ on nano-particle formation.

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REFERENCES


INTRODUCTION

Secondary aerosol particles form in the atmosphere through gas-to-particle conversion. Both inorganic and organic gases emitted from biogenic and anthropogenic sources get oxidised in the atmosphere, which significantly lowers their saturation vapour pressure (Kroll and Seinfeld 2008). Low-volatility compounds then condense onto pre-existing aerosol particles or participate in New Particle Formation (NPF), which is a process of molecular cluster creation and their subsequent growth (Kulmala et al. 2013). About half of secondary particle mass constitutes of organic compounds, which is referred to as Secondary Organic Aerosol (SOA) (Jimenez et al. 2009). The condensation of organic vapours (SOA formation) is believed to be a critical process for the growth of small particles to the bigger sizes at which they can act as cloud condensation nuclei (CCN) and affect the climate processes (Riipinen et al. 2011, Tröstl et al. 2016).

New Particle Formation occurs throughout the atmosphere in the boundary layer and also in the free troposphere (Zhang et al. 2012). It is known that, in most regions, sulphuric acid (SA) is one of the main precursors for the newly formed clusters (Paasonen et al. 2010). In addition to water, it was shown that basic molecules, such as amines and ammonia, are required for stabilisation of SA clusters (Kulmala et al. 2014 and reference therein). When small clusters are formed, their survival is dependent on the available condensing vapours, otherwise the particles are lost by coagulation to the bigger pre-existing particles (Kulmala et al. 2013). In the boreal forest, it was found that the growth of particles can be potentially accounted for by the condensation of Highly Oxygenated Molecules (HOMs) from monoterpene oxidation (Ehn et al. 2014). Since then, the formation of HOMs from monoterpene, in particular from α-pinene oxidation has been extensively studied. Recently, the role of HOMs in the initial steps of NPF has been also recognized (Bianchi et al. 2016, Kirkby et al. 2016).
It has been proposed that HOMs are first-generation products of oxidation of monoterpenes (Ehn et al. 2014, Jokinen et al. 2014, Rissanen et al. 2015). Monoterpenes react with hydroxyl radical (OH), ozone or nitrate radical (NO$_3$) and, in most cases, rapidly form peroxy radicals (RO$_2$). After that, the oxidation can propagate further through intramolecular H-shift, and addition of molecular oxygen, a process also called autoxidation (Crounse et al. 2013). The HOMs are typically measured using NO$_3$-based chemical ionization mass spectrometry and peroxy radicals as well as closed-shell monomer and dimer species have been directly detected. HOM formation from second and higher generation oxidation steps is also possible, though this takes place on longer timescales and has so far received less attention.

In urban polluted areas, the contribution of biogenic molecules to total volatile organic compounds (VOC) is quite small. Out of anthropogenic VOC, aromatic precursors are the most efficient SOA precursors (Kroll and Seinfeld 2008), typically constituting 15-20% of total VOCs in urban and industrial environments (Calvert 2002). Aromatic VOC are toxic and carcinogenic pollutants that originate from traffic, solvent use and fires. In contrast to monoterpenes, which show higher HOM yields upon reaction with ozone, primary emitted aromatic molecules, such as benzene and toluene, react essentially only with OH (Atkinson and Arey 2003). In most reactions, OH attaches to the aromatic ring forming a phenolic compound or a RO$_2$ radical after addition of oxygen. The phenolic compounds are generally more reactive with OH, and multi-generation oxidation products in aromatic systems were identified as significant in SOA formation (Ng et al. 2007). In aromatic systems, HOMs are potentially formed from isomerization of bicyclic RO$_2$ or through oxidation of phenolic products and/or epoxide reactions. HOM formation in oxidation of benzene and other aromatic molecules has been recently shown in flow tube and chamber experiments (Garmash et al. in preparation, Molteni et al. 2016).

In the real atmosphere, the sources of aromatic compounds are the same as of NO$_x$ (NO$_x$ = NO+NO$_2$). The reactions with NO and NO$_2$ alter the branching ratios of the oxidation products and affect their volatility distribution. Previous studies have indicated the production of various nitro-aromatic compounds in multi-step oxidation in presence of NO$_2$ (Jenkin et al. 2003). Nitro-aromatics efficiently absorb the solar energy and when present in the cloud droplets, can affect the Earth’s radiation balance.

The presence of NO was shown to alter the product distribution in aromatic oxidation, for example, increase the fraction of ring scission products (Birdsall and Elrod 2011). The HOM distribution in the boreal forest was also shown to be affected by NO through the reaction with RO$_2$ and formation of organic nitrate (Yan et al. 2016). Since the RO$_2$ radicals are central to all organic oxidation, similar effects of NO may be expected for the aromatic system. Existing chemical mechanisms, in most cases, predict the decomposition of RO$_2$ from aromatic oxidation upon reaction with NO (Jenkin et al. 2003). Birdsall and Elrod (2011), however, experimentally detected bicyclic organic nitrate from TMB oxidation. Recent study of benzene oxidation has shown the evidence of nitrogen-containing HOM formation when NO is introduced to the system, which are potentially highly oxygenated organic nitrates (Garmash et al. in preparation). Aromatic SOA studies in presence of NO$_2$ have shown that at higher NO$_2$ conditions, the SOA formation is suppressed, suggesting that NO$_2$ may inhibit the formation of lower volatility products (Ng et al. 2007).

In this study, we have conducted a series of chamber experiments at the Cosmic Leaving OUtdoor Droplets (CLOUD) chamber located in European Centre for Nuclear Research (CERN, Geneva, Switzerland). The main aim of the study was to elucidate the effect of NO$_x$ on the distribution of HOMs and the effect of these molecules on formation and growth of small aerosol particles. The results obtained from this intensive campaign will help us better understand the urban chemistry and the connection of anthropogenic emissions on the formation of harmful photochemical smog.

METHODS

The experiments were conducted in the CLOUD experiment chamber during CLOUD11 campaign in autumn 2016. The CLOUD chamber is a continuous flow 26.1m$^3$ stainless steel reactor. The inner walls of
the chamber are electrically polished and the bath gas is made up from cryogenic liquid N\textsubscript{2} and O\textsubscript{2} mixed at a 79:21 ratio. The chamber is operated at very clean conditions (contaminants concentration < pptv), which allows us to investigate the chemistry of the initial steps of NPF (Kirkby et al. 2016).

The OH was produced from photolysis of ozone at 248nm. In addition, UV-sabre (385nm) to photolyse NO\textsubscript{2} to NO and Hamamatsu UV (Xe & Hg, 250-450nm) lights to increase O\textsubscript{3}/NO\textsubscript{2} photolysis were used. The chemistry and nucleation potential of aromatic compounds have been investigated in presence of sulphur dioxide (SO\textsubscript{2}, to produce sulphuric acid) and ammonia, as these gases are always present in the urban environment. The experiments were conducted at near-atmospheric pressure and 22\textdegree{}C, with RH of 60\%. We have investigated the oxidation of toluene, 1,2,4-trimethylbenzene and naphthalene, and the mixture of them. The experimental details for individual VOCs are presented in Table 1. Lights, ozone and the concentration of organics were varied to simulate a wide range of conditions.

<table>
<thead>
<tr>
<th>Toluene, ppb</th>
<th>1,2,4 - TMB, (\text{ppb})</th>
<th>Naphthalene, (\text{ppb})</th>
<th>NO\textsubscript{x}, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>26</td>
<td>0</td>
<td>0</td>
<td>2-10</td>
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<td>0</td>
<td>2.5</td>
<td>0</td>
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<td>0</td>
<td>4-8</td>
<td>0</td>
<td>4</td>
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<td>0</td>
<td>0</td>
<td>0.15-1.4</td>
<td>1.4-20</td>
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<tr>
<td>0</td>
<td>0</td>
<td>1.2-4</td>
<td>1.4-20</td>
</tr>
</tbody>
</table>

Table 1. The sampled systems of single VOC in presence and absence of NO\textsubscript{x}.

The HOM composition and the concentration of sulphuric acid were monitored using Chemical Ionisation Atmospheric Pressure interface Time-Of-Flight mass spectrometers (CI-API-TOF). In addition, API-TOF (no ionization) was deployed to measure the composition of the negative ions. A proton-transfer mass spectrometer (PTR-TOF) was used to detect the parent aromatic compounds as well as the lower oxidised products. Specific monitors measured ozone and NO\textsubscript{x} concentrations. In addition, the concentration of NO\textsubscript{2} and glyoxal/methylglyoxal, fragmentation products of aromatic oxidation, was monitored using cavity enhanced Differential Optical Absorption Spectroscopy (CE-DOAS).

RESULTS & CONCLUSIONS

![Figure 1: The distribution of HOM detected by CI-API-TOF in toluene oxidation experiment in absence and presence of NO\textsubscript{x}.](image)

In the experiments at the CLOUD chamber, we observed the formation of nitrogen-containing HOMs. Figure 1 shows the effect the addition of NO\textsubscript{x} had on the distribution of the oxidation products in toluene system. On the lower panel, we can see that the reduced contribution of dimers can be observed when NO\textsubscript{x} is present. This is likely due to a reduced probability of RO\textsubscript{2}+RO\textsubscript{2} reaction leading to dimer as peroxy and
other radicals react with abundant NO and NO\textsubscript{2}. In addition, lower panel shows an increased contribution of peaks with odd mass-to-charge ratio, which indicates those molecules contain nitrogen. Similarly to Garmash et al. (in preparation), nitro-phenol and nitro-cresol were detected by CI-API-TOF as major peaks and were not included in Figure 1.

Previous studies of NO\textsubscript{x} chemistry at CLOUD chamber has shown a formation of NO\textsubscript{3} radical. As phenolic compounds may react with NO\textsubscript{3} as fast as with OH, the effect of NO\textsubscript{3} on HOM composition will be discussed. The reaction with NO\textsubscript{3} is likely more important for naphthalene, as a monoaromatic molecule - NO\textsubscript{3} adduct rapidly decomposes (Ziemann and Atkinson 2012).

The CLOUD chamber makes it possible to simulate the conditions of the atmosphere and study the chemical reactions at atmospherically-relevant concentrations. The wide range of conditions was sampled by varying the concentration of OH, NO and NO\textsubscript{2}. HOM composition as a function of NO\textsubscript{x} will be presented. The effect of NO\textsubscript{x} on nucleation and growth in aromatic system will be presented by Xiao et al. (this abstract collection). The results of this study will give an insight into chemistry of aromatic molecules and help us to identify the key chemical pathways related to the formation of particles in urban environments.

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REFERENCES

Jimenez, J. L., M. R. Canagaratna, et al. (2009), Science 326, 1525.
EFFECT OF ORGANIC CONTENT AND HUMIDITY ON THE STRUCTURE OF ATMOSPHERIC NANOPARTICLES: A MOLECULAR DYNAMICS STUDY

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INTRODUCTION

Atmospheric particles contain usually both inorganic and organic compounds (Calvo \textit{et al.}, 2013). Although inorganic species have been studied and are understood reasonably well, the great variety of organic species involved in atmospheric processes has limited our understanding of the physical and chemical behavior of organic aerosol (OA). The fact that only a small fraction of organic compounds present in atmospheric aerosol has been identified so far (around 10%) (Goldstein and Galbally, 2007), in combination with the many different chemical transformations that these undergo in the atmosphere considerably restricts their study (Seinfeld and Pandis, 2006). For this reason, in laboratory experiments, field measurements and modeling selected organic compounds are used as representative of the various OA types. Quite recently, molecular simulation methods, such as molecular dynamics (MD), have been employed to obtain microscopic-level information about the structural and physicochemical properties of atmospheric aerosols. The systems studied by MD employ chemical compounds found in the atmosphere, but these are often confined to only organic species and water (Darvas \textit{et al.}, 2013). In our study here, we consider a more realistic particle composition focusing on nanoparticles composed of both organic (such as pinonic acid and large alkanes) and inorganic compounds (represented here by sulfate and ammonium ions and water). The MD simulations are carried out in the isothermal-isobaric (NPT) ensemble and allow for the formation of multicomponent nanoparticles likely to be observed in the atmosphere. We provide results for the predicted morphology of these nanoparticles (in addition to issues related with their size and local density variation), intermolecular pair correlation functions, and mobility of the constituent species. The MD simulations also provide information about the phase state of these nanoparticles and the potential presence of the organics at the gas-particle interface. We also investigate the impact of relative humidity on these properties and the effect of the type of organic compound on nanoparticle morphology and structure by considering oxygenated and non-oxygenated organic molecules or combinations. Our results can be used to better understand the degree of participation of various organic compounds on heterogeneous chemical reactions as well as to understand their lifetime in the particulate phase due to oxidation.

SIMULATION CONDITIONS

The base-case simulation system was composed of 10 molecules of cis-pinonic acid (cpa), 200 sulfate ions, 400 ammonium ions, 400 water molecules, and 237 nitrogen and 63 oxygen molecules (the gas phase molecules, air). The initial configuration was designed with the help of the MAPS (MAterials and Process Simulation) platform, and then its potential energy was minimized for the system to get rid of
atom overlaps. The subsequent MD simulation was performed in the NPT statistical ensemble using the Nosé-Hoover thermostat-barostat to keep the values of temperature $T$ and pressure $P$ constant, equal to 310 K and 1 atm, respectively. Standard periodic boundary conditions were imposed in all three space directions. The total simulation took 60 ns. A temperature of 310 K was chosen as a compromise between computational efficiency and physical relevance. Test simulations at room temperature ($T = 298$ K) with smaller systems (to speed up run execution) did not reveal any remarkable differences from those at 310 K. For the integration of the equations of motion we used velocity-Verlet integration, as incorporated in the open-source software package LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator), with the integration step equal to 1 fs. Trajectory snapshots for the subsequent post-processing analysis were saved every $10^4$ integration steps. For all molecules and ions the O.P.L.S. (Optimized Potentials for Liquid Simulations) force field (Jorgensen et al., 1988) was adopted, with the exception of water molecules for which the SPC/E model (Berendsen et al., 1987) was utilized. We further used the SHAKE algorithm (Ryckaert et al., 1977) to maintain the values of bond length and bond angle for water and air molecules fixed. Electrostatic interactions were computed with the P.P.P.M (Particle-Particle-Particle-Mesh) method, where electrostatic energy and forces were computed in Cartesian space up to 12 Å and in reciprocal Fourier space beyond that. For the van der Waals forces a 12-6 Lennard-Jones potential was chosen, with a cut-off radius equal to 12 Å. As far as the mixing rules and the treatment of 1-4 interactions are concerned, we adopted the rules implemented in the O.P.L.S. force field.

In the course of the MD simulation and starting from the initial, minimum-potential energy configuration generated randomly by MAPS, we observed initially the formation of small nanoparticles, which next collided one with each other and aggregated giving rise to bigger particles, until eventually only one single nanoparticle was formed. It took approximately 30 ns for the final nanoparticle to form and equilibrate, thus only the last 30 ns of the accumulated trajectory were used for the subsequent calculation of the physical properties of interest here.

RESULTS AND DISCUSSION

The formed nanoparticle was not a perfect sphere but more like an ellipsoid. To quantify its size, we computed the three eigenvalues of its mass moment-of-inertia tensor. Their average values were found to be equal to 1.63, 2.03 and 2.83 nm while the corresponding average nanoparticle mass density was estimated to 1.48 g cm$^3$. These imply that our atmospheric nanoparticle had an equivalent spherical diameter equal to 4.2 nm. The local density of the simulated nanoparticle as a function of distance from the particle’s center-of-mass is displayed in Figure 1. An almost uniform distribution inside the particle is

![Figure 1. Radial profiles of the local mass density of the four different chemical compounds that participate in the formed nanoparticle, as well for the total. The profile for pinonic acid molecules is magnified by a factor of ten for better visualization.](image-url)
observed for all species, with the exception of cis-pinonic acid which prefers to be closer to the surface of the nanoparticle leaving the core of the nanoparticle with practically zero organic content in this case. The peaks observed in Figure 1, especially on the profiles of the sulfate and ammonium ions, indicate a non-liquid phase. Ions prefer to occupy the central region of the nanoparticles under these conditions. Water molecules, on the other hand, prefer the space near the surface of the nanoparticle, with the peaks in their local mass density profile being at the same radial positions as those of the sulfates and cis-pinonic acid. This can be easily understood, since sulfates exhibit a strong affinity with water through the formation of hydrogen bonds; and the same is true for cis-pinonic acid through its carboxyl group. These favorable interactions are further confirmed by inspecting the corresponding radial pair correlation functions. The presence of the pinonic acid molecules away from the particle’s core was further confirmed by computing the distribution density of the distances of the centers-of-mass of the organic molecules from the center of the nanoparticles.

To estimate more precisely the local composition of the nanoparticle, we divided the space inside the nanoparticle into three sub-ellipsoidal parts: the core region, the intermediate area (having the shape of a donut), and the external region (corresponding practically to the free surface of the particle). The majority of cis-pinonic acid molecules (more than 70%) reside in the surface area; none of them could be traced in the core region of the particle. In contrast, sulfate and ammonium ions were present in all areas, with the majority located in the intermediate area. Water molecules were also found in all three areas, but most of them (roughly 70%) were observed to be in the surface area. We also analyzed the mobility of all molecular species inside the nanoparticle. Sulfate and ammonium ions were found to be relatively slowly moving, most likely due to their strong electrostatic interactions with themselves; cis-pinonic acid molecules, on the other hand, exhibited considerable mobility. The least mobility of all species was exhibited by water molecules due to their strong favorable interactions with all species inside the nanoparticle.

In order to study how non-oxygenated organic molecules partition in atmospheric aerosol nanoparticles, we carried out additional NPT MD simulations where cis-pinonic acid was replaced by an n-triacontane, a normal alkane with thirty carbon atoms (n-C_{30}H_{62}). The final nanoparticle consisted of 10 n-C_{30}H_{62} molecules, 200 sulfate ions, 400 ammonium ions and 399 water molecules, and was found to exhibit several similarities but also some striking differences compared to the cis-pinonic acid containing nanoparticle. For example, the core region was slightly smaller in size (it extended up to up 8 Å from the center-of-mass of the nanoparticle) and it contained no alkane molecules. Overall, we found evidence for the co-existence of two phases in the nanoparticle: one rich in inorganic species and water molecules, and another made up almost exclusively of the alkane molecules. The preference of alkanes to form a separate phase can be explained by their poor affinity with all other molecular species in the nanoparticle. Furthermore, being highly hydrophobic, alkanes and water do not mix, which enhances segregation. Even more interesting is the finding that n-triacontane molecules prefer to form some highly ordered structures at the outer surface of the nanoparticle in the form of a lamellar structure. We further clarify that due to their long size, part of the alkane molecules are found in the intermediate region. The formation of the ordered, semi-crystalline structure of alkane molecules reduces their mobility; moreover, their unfavorable interaction with water (which now tends to reside in the “inorganic” area of the nanoparticle) facilitates the mobility of the inorganic compounds.

We also examined the effect of increased water content (humidity) in such nanoparticles and the impact of the total organic mass on local structure, particle phase, and molecular mobility. As expected, increasing humidity “softens” the structure and increases the mobility for both inorganic and organic species, since water molecules are present everywhere in the particle. The nanoparticle becomes softer also when the oxygenated organic mass is increased. Simulation results with mixtures of oxygenated and non-oxygenated molecules indicate the existence of at least two organic phases in the nanoparticle: the first consists of the non-oxygenated molecules which are found to form well-organized structures while the second contains the oxygenated organic mass and the inorganic species. Now, oxygenated organic mass can also be found deeper inside the nanoparticle (even in the central region) with water molecules being displaced at the intermediate region.
CONCLUSIONS

We have presented MD simulation results of multicomponent atmospheric nanoparticles under atmospherically relevant conditions for particles containing both organic and inorganic components and have investigated their local composition, structure, density and mobility. Depending on the degree of inter-molecular interactions at the atomic level, significant differences are observed both in the local motion of the various compounds and their degree of self-organization inside the nanoparticle. Oxygenated organic molecules are predicted to prefer to occupy the area near the surface of the nanoparticle (especially under increased humidity conditions) thus lending themselves more accessible to oxidizing agents. Increasing the relative population of oxygenated organic mass seems to help them distribute everywhere (thus also more uniformly) in the nanoparticle. The fraction of organic mass that resides in the particle core seems to be protected by oxidation reactions. Furthermore, in the case the nanoparticle contains a mixture of oxygenated and non-oxygenated organic molecules, the oxygenated component prefers to occupy the interior of the nanoparticle whereas the non-oxygenated fraction its surface area. Such a non-uniform nanoparticle structure leads to the “protection” of the oxygenated organic mass and allows non-oxygenated organic molecules to participate in heterogeneous chemical reactions. It appears that the degree of hydrophobicity of the organic content, its mass fraction and the level of humidity strongly influence the thermodynamic phase state of the nanoparticle (solid-like versus gel-like) and in some cases can lead to the formation of separate (segregated) phases. Our simulations provide new insights regarding interactions and species kinetics in gas-particulate matter with important implications for studies of heterogeneous chemistry and lifetime of atmospheric organic aerosols.

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REFERENCES

NUCLEATION AND GROWTH UNDER HIGH OH CONDITIONS: USING AN OXIDATION FLOW REACTOR AND THE TOMAS BOX MODEL TO LEARN ABOUT THE CHEMISTRY, NUCLEATION, AND NEW PARTICLE GROWTH POTENTIAL OF AMBIENT PINE-FOREST AIR

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Keywords: AEROSOLS, OXIDATION FLOW REACTOR, NUCLEATION, OXIDATIVE AGING.

INTRODUCTION

Volatile organic compounds (VOCs), and semivolatile and intermediate-volatility organic compounds (S/IVOCs), in the atmosphere can undergo oxidative aging to form lower-volatility vapors that can then participate in secondary organic aerosol (SOA) formation (e.g. Robinson et al., 2007). Recent work has shown that some SOA species are major contributors to nucleation (e.g. Riccobono et al., 2014) and growth (e.g. Riipinen et al., 2012) in many parts of the atmosphere. However, controlled nucleation and growth studies have largely focused on single “traditional” SOA-precursor VOCs, such as α-pinene, rather than looking at the nucleation and growth potential of ambient mixtures of VOCs and S/IVOCs. Additionally, SOA-formation studies have traditionally used reaction chambers with residence times of hours (commonly referred to as “smog chambers”), but these experiments can be affected by losses of both particles (e.g. Bian, et al., 2016) and semivolatile vapors (e.g. Krechmer et al., 2016) to the chamber walls, particularly at longer residence times. In order to reduce these losses as well as be able to study SOA formation using ambient air, and for a wide range of oxidant exposures, oxidation flow reactors (OFRs) have been developed (e.g. the Potential Aerosol Mass [PAM] reactor; Kang et al., 2007). OFRs allow for high and variable oxidant concentrations and short residence times (typically ~2-4 minutes), with the purpose of simulating hours to months of equivalent atmospheric aging. Previous field studies with OFRs have focused on aerosol mass formation and aging (e.g. Ortega et al., 2013, 2016; Palm et al. 2016, 2017). To our knowledge, no study to date has focused on nucleation, growth, and size-distribution dynamics in OFRs.

An OFR was deployed during the BEACHON-RoMBAS field campaign (http://cires1.colorado.edu/jimenez-group/wiki/index.php/BEACHON-RoMBAS) that took place in a ponderosa pine forest in Colorado, USA during July-August 2011. A description of the site and a summary of past atmospheric chemistry observations, including during this campaign, is given by Ortega et al. (2014). The field site’s VOC profile is characterized as being dominated by 2-methyl-3-buten-2-ol (MBO) emissions during the day and monoterpenes at night. Estimates of SOA formation from the measured VOCs were compared to the measured aerosol formation in the OFR from SMPS and AMS measurements. It was shown in Palm et al. (2016) that approximately 4.4x more SOA was formed by OH oxidation in the OFR than could be explained by the VOC concentrations. Comparisons to concurrent S/IVOC measurements indicated that SOA formed from S/IVOCs could explain the “missing” aerosol mass.

In this work, we extend the work of Palm et al. (2016) by modelling the actual number size distri-
butions measured after oxidation in the OFR in order to learn about factors impacting nucleation, growth, and size-distribution dynamics. These factors include gas-phase and heterogeneous chemistry rates, product volatility distributions, and condensation accommodation coefficients. To our knowledge, this is the first time size distributions from an OFR have been thus investigated.

METHODS

The BEACHON-RoMBAS field campaign provided a variety of measurements that informed our modelling work. An OFR sampled ambient air with residence times of ~2-4 minutes. The OH in the OFR was generated from the photolysis of ambient H$_2$O, O$_2$, and O$_3$ using 185 and 254 nm light produced by two low-pressure mercury lamps (“OFR185” mode). The typical exposure cycle for the OFR consisted of six 20-minute-long settings of varying lamp intensities (and thus varying OH exposure concentrations). The example OH exposure discussed in the results section (Figure 1) occurred at night, when monoterpenes dominated the VOC profile. This example represents an estimated OH exposure of 3.5x10$^{10}$ molec s cm$^{-3}$, which corresponds to an equivalent (eq.) age of 0.27 days. Ambient aerosols and aerosols after oxidation in the OFR were measured using an SMPS and AMS, ambient VOCs and VOCs after OFR oxidation were measured with a PTR-TOF-MS, a Thermo Environmental Model 43C-TLE measured ambient SO$_2$ concentrations, and a thermal-desorption electron impact mass spectrometer (TD-EIMS) measured ambient concentrations of S/IVOCs (Palm et al., 2016). Ambient meteorological data such as temperature and RH were also measured. The OFR was operated on top of the measurement trailer, at ambient temperature and RH and with a large inlet to avoid loss of sticky species.

We use the TOMAS-VBS box model (Bian et al., 2016) to simulate the aging of atmospheric gases in the OFR chamber. We allow for 40 size bins (covering dry diameters of 1 nm to 10 µm) and 6 volatility bins from C*$_{1}=1x10^{-4}$–1x10$^{6}$ µgm$^{-3}$ in the model. TOMAS simulates nucleation, condensation, and coagulation as well as a simple aging scheme that moves species down in volatility upon reaction with an OH molecule (Bian et al., 2016). We include a simple OH-caused fragmentation scheme for the lowest-volatility material to account for gas-phase fragmentation. The simulations shown in Figure 1 assume the nucleation scheme and multicomponent prefactor (nucleation rate, k$_n$) of Riccobono et al. (2014), that each reaction with an OH molecule leads to a 2-decade volatility bin drop, that the oxidation reaction rate of VOCs (k$_{OH,TERP}$, here assumed to be monoterpenes only) is that for α-pinene (Atkinson and Arey, 2003), that the oxidation reaction rate (k$_{OH}$) of lower-volatility material is that of aromatics (Jather et al., 2014), and that is no heterogeneous chemistry. We further run simulations (not shown) with a simple heterogeneous oxidation scheme. We initialize each model run using the available ambient measurements.

CONCLUSIONS

Figure 1 shows the SMPS-measured and model-output initial (panel a) and final (panel c) number distributions and derived initial (panel b) and final (panel d) volume distributions for an example OH exposure of eq.age 0.27 days. The model simulation labeled ‘model α = 1.0’ indicates a simulation in which the accommodation coefficient (α) is assumed to be 1.0 for all particle sizes. The model simulation labeled ‘model α = 0.1’ indicates a simulation in which α = 1.0 for particles between D$_p$ = 1–60 nm and α= 0.1 for particles with D$_p$ > 60 nm. The simulation with α = 1.0 for all particle sizes overestimates the growth of the accumulation mode and underestimates the growth of particles in the nucleation mode. It also slightly underpredicts the peak diameter in the nucleation mode. Manipulating k$_{OH}$, initial volatility distributions, and aging rates were not sufficient to decrease the model predictions of growth of the accumulation mode to reasonably match the measurements, particularly the limited growth of the accumulation mode.
Figure 1: Measurement to model comparisons of (a) initial number distributions, (b) initial volume distributions, (c) final number distributions, and (d) final volume distributions for an example OH concentration (eq. age 0.27 days). The labels ‘model α = 1.0’ and ‘model α = 0.1’ refer to the model simulations where the accommodation coefficient, α, is assumed to be 1.0 for all particle sizes and where α is assumed to be 0.1 for particles larger than $D_p = 60$ nm, respectively.

On the other hand, the simulation with $α = 0.1$ for $D_p > 60$ nm closely matches the measured final volume, with only a slight overestimate in the nucleation mode volume. Further, this simulation predicts the peak diameter in the nucleation mode more closely than the ‘model alpha = 1.0’ simulation does. By forcing $α$ to be 0.1 for larger particle sizes, we impose a limitation on the rate of gas-phase uptake by the larger particles. We find that other OH exposures examined (not shown) also require some sort of vapor-uptake limitation for pre-existing accumulation-mode particles in order to replicate the observed particle growth, which was most often characterized by a large increase in the nucleation mode and very little increase in the accumulation mode. Rippinen et al., 2012, estimates that particle-phase transport may affect particle growth at particles sizes larger than $D_p = 50$ nm, due in part to increasing particle viscosity seen for increasing particle size (Virtanen et al., 2010). We further find that modelling increasingly higher OH exposures (not shown) begins to not match measurements unless a simple heterogeneous oxidation scheme is used for all particle sizes, consistent with the expectation that fragmentation appears to be occurring in the reactor. In this presentation, we will show additional results where we search the parameter spaces of $k_m$, $k_{OH}$, heterogeneous chemistry effective reactive uptake coefficient ($\gamma_{OH}$), and $α$ in order to determine what set(s) of parameters best fit the wide range of OH exposures used during BEACHON-RoMBAS.

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REFERENCES


BEACHON-RoMBAS, http://cires1.colorado.edu/jimenez-group/wiki/index.php/BEACHON-
RoMBAS, date accessed Jan 24, 2017.


QUANTIFYING OLIGOMERIZATION IN ORGANIC AEROSOL THROUGH DESORPTION THERMOGRAM MODELING

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INTRODUCTION

Atmospheric aerosol particles adversely affect visibility and health, and they influence climate (e.g. Pöschl, 2005). In particular the overall effect on climate is possibly strong yet highly uncertain (IPCC, 2013). Sub-micron particles are of particular interest, as they often occur in high number concentrations and are able to act as cloud condensation nuclei (CCN), thus indirectly affecting the Earth’s radiation balance (Lee et al., 2013). One of the most important constituents of these aerosol particles is organic matter, making up 20% to 90% of their mass (Zhang et al., 2007). Organic aerosol can be emitted directly (primary organic aerosol) or formed from gas-phase precursors (secondary organic aerosol, SOA), which are typically the products of the oxidative processing of volatile organic compounds (VOC), such as biogenically emitted isoprene and monoterpenes. The condensation or reactive uptake of these products typically explains 90% of new particle growth to CCN within the boundary layer (Ripinen et al., 2012). In atmospheric models, the growth of SOA particles is typically described by equilibrium partitioning between gas and particle phase, based on the volatility of the involved compounds (Donahue et al., 2011). However, these models have typically underpredicted observed SOA loadings (e.g. Heal et al., 2005; Dzepina et al., 2009), and it was found that SOA evaporates more slowly than would be expected from the volatility distributions derived from SOA growth experiments (Vaden et al., 2011). The inability of commonly applied equilibrium partitioning models to replicate the observations may stem from an underprediction of low volatility material, either from inaccurate descriptions of gas-phase radical chemistry (e.g. Ehn et al., 2014) or multiphase accretion chemistry (e.g. Surratt et al., 2006), or invalid assumptions of particle phase state (Virtanen et al., 2010), or a combination of these possibilities. Also diffusion limitations within the particles could thus inhibit evaporation (Cappa and Wilson, 2011). As for the underlying mechanisms, recent experimental and modeling studies indicate a major role of oligomerization, which occurs rapidly (within minutes) upon SOA formation, and that oligomer decomposition indeed controls SOA evaporation rates (Roldin et al., 2014; Kolesar et al., 2015b).

Recent advances in mass spectrometric techniques allow us to measure aerosol molecular composition at sufficiently high time resolution to access those molecular-scale mechanisms. One such technique is the Filter Inlet for Gas and AERosol (FIGAERO), coupled to a high-resolution time-of-flight chemical ionization mass spectrometer (CIMS) (Lopez-Hilfiker et al., 2014). Using the FIGAERO, the molecular composition of a major fraction of an organic aerosol sample can be measured as a function of time and temperature. The resulting composition-resolved thermograms (signal from desorbing compounds vs. ramped temperature) show that a substantial fraction of SOA material is present at a state of lower volatility than the volatility suggested by the composition of the molecules that desorb upon heating, supporting the hypothesis of the pivotal role of oligomer formation and decomposition in determining SOA properties (Lopez-Hilfiker et al., 2016).
In this study, we developed a model to simulate the temperature-controlled evaporation of organic aerosol in the FIGAERO. We apply the model to FIGAERO measurements of SOA that was formed in chamber experiments from the oxidation of monoterpenes (α-pinene and Δ3-carene), with the goal of quantifying the kinetics that govern the formation and decomposition of oligomers.

METHODS

In our study, we aimed at providing a model description for the particle-phase measurements using the FIGAERO, i.e. the desorption of molecules from an aerosol sample that had been collected on a PTFE filter, while exposed to a flow of clean N₂, and their subsequent transport into the CIMS. The temperature of the N₂ flow was usually ramped, from room temperature up to 200 °C. A detailed description of the method is provided in Lopez-Hilfiker et al. (2014). We used a variety of experiments to determine model parameters, including desorptions following the direct injections of calibrant solutions onto the filter, and isothermal desorption experiments (e.g. at room temperature). Eventual application of the model was to SOA formation experiments conducted during an intensive measurement campaign at the Pacific Northwest National Laboratory’s 10.6 m³ environmental chamber (e.g. D’Ambro et al., 2017).

The model consists of a set of differential equations. The desorption rate for a certain compound i from a deposited aerosol particle is described using the Hertz-Knudsen equation (Cappa et al., 2007), i.e. mainly dependent on the compound’s absolute vapor pressure (C'), an evaporation coefficient (α) and the condensed phase surface area. The resulting rate is reduced by multiplying with the mole fraction of the compound in the particle phase, to account for Raoult’s Law, and by a factor that accounts for diffusion limitation both within the particle and into the gas-phase. Two additional terms describe the production of molecules of compound i by the dissociation of oligomers and their loss by formation of oligomers. They are inspired by Kolesar et al. (2015a) and are temperature-dependent as in Arrhenius’ equation.

RESULTS & CONCLUSIONS

Our model output generally produced thermogram peaks similar to those observed in FIGAERO experiments. Disregarding oligomerization at first, the main factors that determined the peak position and shape were: particle-phase diffusivity, expressed as a reduction in α (e.g. Saleh et al., 2013), C', the enthalpy of vaporization ΔH, and the parameters governing vapor-surface interactions, comprising a time scale τ and an equivalent wall organic aerosol concentration C_w. Through a set of isothermal evaporation experiments, we determined τC_w on the order of 5 mg m⁻³ s⁻¹, agreeing with previous experimental findings on interactions of organic vapors with PTFE surfaces (Matsunaga and Ziemann, 2010). Figure 1 shows a model application to the desorption thermograms of a solution containing monocarboxylic acids, using literature values for C’ and ΔH (Lopez-Hilfiker et al., 2014) and α = 1. It shows good overall agreement. The modeled peak position is sensitive to both C’ and ΔH, e.g. a shift by ~10 °C for a change in C’ by a factor of 5. The observed divergence from experimental results of less than 10 °C is thus well within uncertainties common in determining C'. Similar reasoning applies for uncertainties in ΔH, which also affects the steepness of the peak’s slope and hence width.

When sampling SOA using the FIGAERO on the other hand, a substantial fraction of the signal for the majority of compounds desorbed at higher temperatures than their elemental composition would suggest. The corresponding thermograms usually exhibited an initial peak, followed by a plateau towards higher temperatures, or even a second peak (Lopez-Hilfiker et al., 2016). Using our model, we are now able to simulate these more complex peak shapes, when we include the oligomerization terms, and use the rate constants and activation energies that control oligomer formation and dissociation as free parameters in fitting the observed thermograms.
As a result, we gain a quantitative insight into the dynamics of the reversible oligomerization reactions occurring in SOA, broken down into the desorbing molecular compositions, that in many cases were also measured when sampling directly from the gas-phase.

Figure 1. Comparison of experimental results from injecting a solution containing monocarboxylic acids (circles) with model results (lines).

We expect that the new information gained from this approach will greatly improve our understanding of the gas- and particle-phase organic chemistry that control organic aerosol dynamics and properties, and consequently improve the performance of existing and future model frameworks.

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REFERENCES


ATMOSPHERIC PARTICLES FROM UNRECOGNIZED ATMOSPHERE-LAND INTERACTIONS

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INTRODUCTION

Novel methods of chemical imaging facilitate in-depth studies of particles multi-phase chemistry and provide experimental means to improve fundamental knowledge of particle effects on cloud microphysics, particles’ dependence on variables (e.g., RH, temperature, multiphase reactions) and to distinguish the chemistry of natural and anthropogenic particles (Laskin et al, 2016). This presentation will highlight our recent chemical imaging studies of atmospheric particles that are directly ejected from environmental surfaces (Wang et al, 2016; China et al, 2016). The atmospheric processes associated with these particles and their impacts on environment and climate remain insufficiently understood, even at the phenomenological level, largely due to incomplete information on the physicochemical properties of particles. We will present selected studies where chemical imaging provided key advances to examine physicochemical properties of particles related to these unrecognized processes of particle ejection and transformations in the atmosphere.

METHODS

Scanning electron microscopy (SEM), micro-spectroscopy (energy dispersed analyzer of X-rays, EDX), and scanning transmission X-ray microscopy (STXM)/near edge X-ray absorption fine structure spectroscopy (NEXAFS), were used to study multiphase atmospheric chemistry of field and laboratory particles using chemical imaging (elemental and molecular group mapping) (Laskin, 2010; Moffet et al, 2010a). SEM coupled to EDX microanalysis was used for analysis of particle morphology, size, elemental composition, and internal structures with nanometer lateral resolution. Operation of SEM in computer-controlled mode (CCSEM) permits routine analysis of hundreds-to-thousands of particles deposited on substrates and provides statistically significant data on particle-type populations. Environmental operation of SEM (ESEM) allowed real-time imaging of particle hygrosopic transformations.

Synchrotron-based X-ray microscopy (STXM/NEXAFS) enabled chemical imaging of particles with advanced speciation of carbon bonding and chemical characterization of chemical bonding and oxidation states of common elements in atmospheric particles (e.g., C, N, O, S). Selected features of NEXAFS spectra indicative of specific element functionalities were used to construct particle component maps and for grouping and assessment of particle types and their mixing states (Moffet et al, 2010b).

CONCLUSIONS

Airborne biological particles, such as fungal spores and pollen, are ubiquitous in the Earth’s atmosphere and may influence the atmospheric environment and climate, impacting air quality, cloud formation, and
the Earth’s radiation budget. The atmospheric transformations of airborne biological spores at elevated relative humidity remain poorly understood and their climatic role is uncertain. Using ESEM, we observed rupturing of Amazonian fungal spores and subsequent release of submicrometre size fragments after exposure to high humidity (Figure 1). We find that fungal fragments contain elements of inorganic salts (e.g., Na and Cl). They are hygroscopic in nature with a growth factor up to 2.3 at 96% relative humidity, thus they may potentially influence cloud formation. Due to their hygroscopic growth, light scattering cross sections of the fragments are enhanced by up to a factor of 10. Furthermore, rupturing of fungal spores at high humidity may explain the bursting events of new particle formation in Amazonia. Biological particle emissions are typically linked to atmospheric conditions, such as rainfall, RH, wind, and thunderstorms, that influence daily variations in the number fluxes (Huffman et al., 2012). These atmospheric conditions trigger emission and transformations of biological particles, thus impacting the microbiome of ecosystems at the Earth’s surface.

![ESEM images of ruptured fungal spores and expulsion of submicrometer fragments. Panel (c) shows an example of germination pores of fungal spores as indicated by arrows. Scale bar is 2 μm. (China et al., 2016)](image)

**Figure 1.** ESEM images of ruptured fungal spores and expulsion of submicrometer fragments. Panel (c) shows an example of germination pores of fungal spores as indicated by arrows. Scale bar is 2 μm. (China et al., 2016)

Our other field observations provided evidence of a previously unrecognized mechanism of atmosphere–land interactions that result in the ejection of submicrometre airborne soil organic particles (ASOP) after intensive precipitation (Wang et al., 2016). These observations were corroborated by a separately reported laboratory study (Joung and Buie, 2015) who reported raindrop-induced frenetic generation of bubbles within a layer of surface accumulated water followed by ejection of very fine aerosol upon bubble bursting. Similar to the generation of organic sea spray particles, dissolved soil organic matter (SOM) is aerosolized by the bursting of entrained bubbles at the air-water interface (Figure 2). Molecular constituents of SOM are substantially larger than common atmospheric organics. Therefore, evaporation of water from SOM-containing aqueous mist results in solidification of the resulting ASOP at ambient conditions, as confirmed by the observed glassy, spherical morphology and chemical imaging. This additional, previously unrecognized type of organic aerosol may have significant impacts on the atmospheric environment in areas where soils are exposed to strong, episodic precipitation events such as agricultural systems or natural grasslands.
Figure 2. A schematic illustration of the ‘raindrop’ mechanism generating airborne soil organic particles (ASOP). (1) Raindrops impinging on the soil surface entrain air bubbles into the surface water layer containing dissolved soil organic matter (SOM). (2) The bubbles burst at the air/water interface and eject ASOP that solidify to become glassy particles on drying. The insert in the upper left corner shows a scanning electron micrograph image of glassy ASOP collected at the Southern Great Plains site. (Wang et al., 2016)

Due to their soil-derived composition and substantial content of carbon with sp² hybridization (C=C double bonds), ASOP may contribute substantially to atmospheric brown carbon (Andreae and Gelencser, 2006; Laskin et al., 2015) and its associated light absorption and scattering. ASOP advected aloft may ultimately impact cloud properties and subsequent precipitation. Dynamic ESEM imaging of hydrating ASOP confirmed that they remain water soluble and CCN active. Furthermore, because of their glassy phase, ASOP provide solid surfaces for heterogeneous ice nucleation in cold and mixed-phase clouds.

Future studies should further explore the effects of atmosphere-land surface interactions on particle emissions by assessing the relationship between rainfall intensity and efficiency of particle generation, evaluate and constrain ASOP and biological particles budgets at different geographic areas, describe area-specific variability in particle composition, and quantify their optical and cloud nucleation properties.

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REFERENCES


KINETIC MODEL FOR CONDENSATION-INDUCED RESTRUCTURING OF ATMOSPHERIC SOOT AGGLOMERATES

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Abstract We present a basic model which determines the tendency of a soot agglomerate to restructure as a result of vapor condensation. The restructuring condition is governed by the value of a single dimensionless parameter, which includes the size of the soot spherules, the surface tension and density of condensed liquid, and the vapor supersaturation.

Keywords: soot agglomerates, restructuring, condensation, supersaturation

INTRODUCTION

Soot is a major environmental pollutant which deteriorates air quality and affects human health. Moreover, soot nanoparticles serve as condensation nuclei for atmospheric aerosols, light absorbers and scatterers, impacting the climate (Bond et al., 2013; Shiraiwa et al., 2012). Soot nanoparticles are fractal agglomerates of graphitic spherules mixed with organic or inorganic products of combustion. The optical properties of soot and transport properties of soot in human respiratory tract strongly depend on the morphology of soot agglomerates (Xue et al., 2009; Broday and Rosenzweig, 2011). Therefore, in order to assess the negative impacts of soot on both climate and human health one has to know the microstructure of soot nanoparticles.

When soot nanoparticles are exposed to other organic and inorganic products of combustion process, or to water vapor, they often restructure, evolving from the branched fractal structures to globules (Weingartner et al., 1995; Mikhailov et al., 1998). However, restructuring is not a universal feature, and the same soot may restructure in one vapor, but not in another (Skillas et al., 1998; Chen et al., 2016). It was also shown that the restructuring depend on the amount of condensed vapor (Pagels et al., 2009; Ghazi and Olfert, 2013; Bambha et al., 2013). In our recent work we exposed soot to vapors of various polycyclic aromatic hydrocarbons (PAHs), which have similar chemical structure and properties (Chen et al., 2016). Moreover, we used the comparable amounts of PAHs. However, we found that while some PAHs (e.g. phenanthrene) induced restructuring, other (e.g. anthracene) did not, this is exemplified in Fig. 1. In order to explain this difference a quantitative model of condensation-induced soot restructuring is needed. This work presents the first step towards development of such a model.

METHODS

Here we do not consider the mechanics of the restructuring, which is similar to condensation-induced deformation of nanoporous materials (Gor et al., 2017), but discuss the thermodynamic and kinetic premises for this process. Following the earlier works on soot agglomerates restructuring (Kütz and
Figure 1: SEM micrographs of 350 nm initial mobility diameter soot aggregates: (a) fresh soot (b) coated with anthracene, (c) coated with phenanthrene. While the anthracene coverage does not affect the branched fractal structure of the aggregate, the phenanthrene causes its restructuring to a globule.

Schmidt-Ott, 1992; Weingartner et al., 1995) we assume that restructuring is driven by forces in the joints (gaps) between the spherules. Therefore, we consider two limiting cases of the vapor condensation: (1) the vapor condenses as a uniform liquid film on the surface of the spherules, not causing restructuring, (2) the vapor condenses exclusively in the gap between the spherules, causing restructuring. Left panel in Fig. 2 illustrates these two scenarios.

We consider an agglomerate in the medium consisting of air and a single component supersaturated vapor. We assume that the vapor condenses to the liquid phase and the surface of soot particle solvophobic for the condensate. Since the spherules are small ($R_s \sim 10 - 20$ nm) comparing to the mean free path of the vapor molecules, the condensation takes place in free-molecular regime, irrespective whether the droplet grows on the surface of the spherule or in the gap between the two. The flux of molecules to the surface of the growing droplet is (Seinfeld and Pandis, 2006)

$$J = \frac{1}{4} \alpha A v_T (n_0 - n_{sat}).$$

(1)

Here $\alpha$ is the molecular accommodation coefficient, $A$ is the surface area of the droplet, $v_T$ is the mean thermal velocity of the molecules, $n_0$ is the unperturbed vapor concentration far from the droplet, $n_{sat}$ is the concentration of saturated vapor near the droplet’s surface.

Let $n_{\infty}$ be the concentration of the saturated vapor at the flat surface of liquid at the same temperature $T$. When condensation takes place at a curved surface, $n_{sat}$ in Eq. 1 differs from $n_{\infty}$ due to Kelvin effect. For the condensation on the spherule’s convex surface $n_{sat} > n_{\infty}$ and the driving force for the condensation $(n_0 - n_{sat})$ is smaller than for a flat surface. For the condensation in the gap, the liquid interface can, on contrary, be concave and the driving force $(n_0 - n_{sat})$ can exceed that of the flat surface. For simplicity, we linearize Kelvin equation for $n_{sat}$ for the liquid on the spherule and assume the surface of the liquid droplet in the gap to be flat (see the right panel of Fig. 2). Thus we calculate the volume of the droplet in the gap as a volume of the cylinder with height $2h$ and diameter $2r$ minus the two spherical caps of height $h$; and take $n_{sat} = n_{\infty}$. Within these approximations the condensation problems can be solved analytically. Analytical solutions help to derive the conditions for domination of one of the condensation scenarios: condensation in the gap, which causes restructuring, or condensation on the spherule, which does not cause restructuring.

RESULTS

The amount of condensed liquid is determined by material balance with the flux given by Eq. 1. Integration of the corresponding differential equations for the two geometries shown in Fig. 2 with the natural initial conditions gives for the gap and for the spherule respectively:

$$l = 4 \sin \left[ \arccos \left( 1 - \frac{h}{r} \right) \right],$$

(2)
Figure 2: (Left) Two limiting possibilities for the condensation on a soot agglomerate: the condensate covers the surface of the solid spheres as a uniform film or it covers exclusively the gap between the spheres and does not condense of the spheres surface. (Center) Geometry of the liquid film growing on the spherule. (Right) Geometry of a liquid film growing in the gap between the two solid spheres.

\[
\tilde{t} = 4 \left\{ \frac{\tilde{R} - 1}{\chi \ln \left( \frac{\tilde{R} - \chi}{1 - \chi} \right)} \right\}, \quad \text{where} \quad \chi \equiv \frac{\ell_K}{R_s} \zeta.
\]

These equations are written in the reduced units of length and time: reduced radius of the liquid film \( \tilde{R} \equiv R/R_s \), and thickness of spherical caps \( \tilde{h} \equiv h/R_s \). The reduced time is defined as \( \tilde{t} = \alpha n^2 \eta / R_s \) (Grinin et al., 2011), and \( \eta \) is the concentration in the liquid phase. Parameter \( \ell_K \equiv n \theta / 2 \gamma ) \) is the Kelvin length, which contains the surface tension of the liquid \( \gamma \), \( \theta \) is the Boltzmann's constant. Finally \( \zeta \equiv (n_0 - n_\infty) / n_\infty \) is the supersaturation of the vapor.

The equations written in this form reveal that the competition between the condensation on a spherule and in the gap is determined by a single dimensionless parameter \( \chi \). From Eqs. 2 and 3 we calculated the amount of liquid condensed in two systems as a function of time for various values of parameters \( \chi \) and plotted in Fig. 3. For \( \chi \ll 1 \) the condensation on spherules dominates; when \( \chi \) is increasing, approaching the limit of \( \chi = 1 \), the condensation in the gap is the dominating process. The second scenario causes the restructuring of the agglomerates.

Figure 3: Amounts of vapor condensed in two regions: on a surface of a sphere and in the gap between the spheres. The solutions are shown in reduced units in which the former is a function of a single parameter \( \chi \) and the latter is universal.

In our experiments for PAHs, we found that the PAHs with lower melting temperatures cause restructuring, while the PAHs with higher melting temperature do not (Chen et al., 2016). The former group is also more volatile (Oja and Sunberg, 1998), and therefore had lower supersaturation \( \zeta \) in our experiments. According to Eq. 3, lower \( \zeta \) corresponds to higher \( \chi \). Therefore, the presented theory explains our earlier experimental results.
CONCLUSIONS

The presented model suggests that the tendency of a soot agglomerate to restructure as a result of vapor condensation is determined by the value of dimensionless parameter $\chi$, which includes the size of the soot spherules, the surface tension and density of condensed liquid, and the vapor supersaturation. The latter factor is the most important, since it may vary in a wide range. Our model explains the experimental observations, reported by our group recently (Chen et al., 2016) and due to its simple analytical form, it can be incorporated into atmospheric models to improve simulations of the soot aerosol aging and its impact on direct radiative forcing.

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REFERENCES


SESSION 14:

SUB 10 nm AEROSOL INSTRUMENTATION

Chris Hogan: The development of drift tube ion mobility spectrometry for the analysis of sub 10 nm particles

Markus Leiminger: The nanoTOF: A novel approach to study cluster ions

Daniela Wimmer: Experimental investigation of aerosol particle composition and growth rates

Lauri Ahonen: Characterisation of the effects caused by sample air humidity to the performance of a diethylene glycol based particle size magnifier

Christian Tauber: On the temperature dependence of heterogeneous nucleation of n-butanol vapor on Ag and NaCl particle

Konstantinos Barmpounis: Alternating sign preference in ion-induced nucleation

Juha Kangasluoma: On selected sources of uncertainty in the sub-3 nm particle concentration measurement
THE DEVELOPMENT OF DRIFT TUBE ION MOBILITY SPECTROMETRY FOR THE ANALYSIS OF SUB 10 NM PARTICLES

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Keywords: Mobility Analysis; Nanoparticles; Drift Tube; Condensation Particle Counter

INTRODUCTION

The most common method of inferring particle size distributions in the sub 10 nm range in both laboratory and field studies is through mobility analysis with a differential mobility analyzer-condensation particle counter (DMA-CPC) system. In large part it is the CPC which makes use of this system advantageous; for particles larger than a critical size, CPCs exhibit single particle sensitivity and hence enable size distribution measurement in low concentration environments (McMurry 2000). Conversely, while DMAs enable isolation of particles within a specific mobility window, there are several shortcomings associated with their use, including (1) degradation of device transmission and resolution with decreasing particle size, (2) the need to scan the voltage settings on the instrument for size distribution measurement, making it difficult to apply DMAs to temporally evolving aerosols, and (3) the need to maintain a stable, controlled composition sheath flow in excess of 10 l min⁻¹ or more. Drift tube ion mobility spectrometry (DTIMS) is an alternative approach to differential mobility analysis for the determination of mobility distributions of charged particles and ions (Dugourd et al. 1997; Revercomb & Mason 1975). Largely used in the analysis of explosives (Ewing et al. 2001) and electrosprayed biomolecules (Bohrer et al. 2008), in DTIMS, sampled charged particles and ions are introduced into a tube with an axial electric field at a specific instant in time, thus they migrate through the tube with speeds proportional to their mobilities. The mobility distribution can be inferred from an arrival time distribution function at a detector. Most DTIMS systems are interfaced with electrometers or mass spectrometers for the detection of subnanometer ions or multiply charged particles, and further operate at reduced pressures. This typically makes them incompatible with CPCs. Nonetheless, because DTIMS have resolving powers and transmissions which are relatively insensitive to mobility, and because they can be used to analyze temporally evolving aerosols, there would be advantages in their application to aerosol particle measurements.

Recently we have developed a fluid mechanically gated DTIMS system which can (1) sample charged aerosol particles from grounded systems (most DTIMS systems cannot), (2) function at atmospheric pressure, and (3) be interfaced with an aspirating detector, such as a CPC (Oberreit et al. 2014b). This presentation describes the development and application of this instrument as well as the development of a commercial DTIMS-fast response CPC combination.

METHODS

DTIMS-CPC System: A schematic of the original DTIMS prototype along with the streamlines and isoelectric potential lines at the inlet and outlet (as predicted by simulation) are shown in Figure 1, which is adapted from Oberreit et al (2014b). In the DTIMS system, when voltages are not applied, sample is aspirated into the inlet, where it encounters a counterflow introduced near the outlet and flowing from outlet to inlet. This flow prevents particles from traversing the tube in the absence of voltage. At the start of a measurement, voltages are applied near instantaneously to a series of ring electrodes to create a nearly axial electric field gradient. Charged particles (of the desired polarity) within the sample volume at the time of voltage application will then migrate through the tube with velocities proportional to their
mobilities and thus arrival times (at the outlet) proportional to their inverse mobility/size. At the outlet, particles are then directed via flow into an aspirating detector, such as a CPC. The original DTIMS system, with dimensions displayed in Figure 1, was interfaced with a water based condensation particle counter for proof of concept measurements. The results of these measurements with a 9 kV voltage difference across the DTIMS, sample 1.0 l min\(^{-1}\) of DMA classified particles and with a counterflow of 0.3 l min\(^{-1}\) are shown in figure 2a. Figure 2b displays the experimentally observed and theoretically expected relationship between peak in arrival time distributions and inverse mobility. After initial measurements, improvements to the device have been made; the to-be commercialized version is equipped with a faster response time butanol based CPC (from Kanomax FMT), and is able to make measurements in the 2 nm – 40 nm size range in under 50 seconds (less than 10 seconds for sub 10 nm). Resolving powers in excess of 20 are also attainable with the newer instrument.

Figure 1. (a.) Schematic of the DTIMS prototype system. (b.) Streamlines of flow and isoelectric potential lines predicted from computational fluid dynamics and electrostatics simulations of the inlet. (c.) Streamlines of flow and isoelectric potential lines at the outlet.

Figure 2. (a.) The arrival time distributions for the DTIMS-CPC prototype for DMA selected particles with 9 kV applied across the DTIMS. Circles- experimental measurement; Squares- Multiphysics simulations; Triangles- Analytical modeling. (b.) The peak in arrival time distributions as a function of inverse mobility (1/Z\(_{p}\)), showing a linear relationship. Circles- experimental measurement; Squares-Multiphysics simulations; Triangles- Analytical modeling.
Applications: To date the system has been applied not only in size distribution measurements, but in tandem with a DMA for DMA-DTIMS-CPC measurements (Oberreit et al. 2014a; Ouyang et al. 2015) to determine the hygroscopicity of sub 10 nm particles. Because a DTIMS-CPC is naturally “scanning”, the DMA-DTIMS combination is ideally suited for tandem mobility measurements.

CONCLUSIONS

Though drift tube ion mobility spectrometry has existed as an analytical technique for more than 40 years, its application to aerosol particles is new. In conjunction with a condensation particle counter, DTIMS systems open up new avenues of measurement for sub 10 nm particles.

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REFERENCES


THE NANOTOF: A NOVEL APPROACH TO STUDY IONIC MOLECULAR CLUSTERS USING ION MOBILITY CLASSIFICATION

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Keywords: NUCLEATION, MASS SPECTROMETRY, ION MOBILITY, CLUSTER IONS

INTRODUCTION

In the past years, the understanding of atmospheric new particle formation made an impressive step forward (e.g. Almeida et al., 2013; Schobesberger et al., 2013; Kirkby et al., 2016). New instrumentation, such as the Atmospheric Pressure interface-Time of Flight (APi-TOF, e.g. Junninen et al., 2010) mass spectrometer (MS), enabled the study of the formation of molecular cluster ions from precursors like sulfuric acid, amines, or volatile organic compounds in the earth atmosphere. However, it is still unclear to which extend fragmentation and evaporation of more loosely bonded ligands such as H₂O, ammonia, amines, oxidized organics and others impact the transmission efficiency of cluster ions from ambient pressure to the vacuum.

The high-resolution Time-of-Flight Mass Spectrometer using a novel type of inlet aimed to investigate fragmentation and evaporation processes of loosely bonded ligands from nucleating ionic molecular clusters in the sub 2 nm size range. It addresses the question, whether currently used other instrumentation, such as the APi-TOF-MS, loses weakly bonded ligands from cluster ions during the transition from ambient pressure to the vacuum. Key features of the new nanoTOF are an inlet consisting of an Axial Ion Mobility Classification (AMC) in combination with a Collision Induced Dissociation (CID) cell and a low-fragmentation ion transfer stage guiding the cluster ions into the mass spectrometer. Here, we present first results from experiments investigating the performance of the AMC and CID techniques.

METHODS

This work offers a new approach for the determination of the chemical composition of sub 2 nm atmospheric ionic molecular clusters, using a new and innovative prototype mass spectrometer, further on referred to as the “nanoTOF”. It is based on the soft, low fragmentation transition of molecular ions into the high vacuum of a mass spectrometer as used in the Innsbruck PTR-MS (Hansel et al., 1995) and PTR-TOF (Graus et al., 2010). The “nanoTOF” prototype consists of a high-resolution time-of-flight mass spectrometer (Tofwerk AG, Thun, Switzerland) and a new inlet with an implemented Collision Induced Dissociation (CID) cell for a well-defined control of the degree of fragmentation of the cluster ions. Additionally, the “nanoTOF” inlet features an integrated Axial Mobility Classifier (AMC) of the airborne molecular clusters to be able to monitor the degree of fragmentation of the clusters in the CID cell.

The combination of AMC and CID allows the stepwise fragmentation of ligands from the core ions of the ionic molecular clusters. The AMC makes it possible that only cluster ions with a specific electrical mobility, Z, pass the inlet. Further on, these cluster ions can be subject to collision induced dissociation in the CID cell, where precise variations in E/N (E: electric field strength, N: number gas density) allow a controlled fragmentation and analysis of the cluster ions.
EXPERIMENTAL

For the newly developed “nanoTOF” inlet, the overall ion transmission efficiency from ambient (atmospheric) pressure to the detector of the MS at high vacuum and the resolution power of the electrical mobility classification are two critical parameters that need to be determined experimentally. For the characterization of the new inlet and to test its performance, we used two different experimental setups. The setup for the determination of the overall ion transmission efficiency of the nanoTOF inlet is schematically shown in Figure 1. The core part is the Cluster Calibration Unit (CCU), consisting of a Vienna-type high resolution Differential Mobility Analyzer (UDMA, Steiner et al. 2010) for the size segregation of well-defined, electrospray generated monomobile molecular clusters. Two aerosol electrometers (EM1 and EM2) upstream and downstream of the nanoTOF inlet allow the determination of the size/mass dependent overall ion transmission efficiency.

The AMC in the nanoTOF uses a similar approach as recently presented by Bezantakos et al. (2015) and Tammet (2015): an electric field, opposed to the instrument’s inlet flow, is slowing down the ions, and allows only ions below a certain critical electrical mobility to pass the potential maximum. By continuously reducing the potential barrier, also ions with higher mobilities are allowed to pass. An illustrative set of AMC mobility scans of electrospray generated tetra-alkyl ammonium halide clusters is shown in Figure 2.

Figure 1. Schematic of the experimental setup used to test the performance of the nanoTOF inlet (see text for details).

Figure 2. Characterization of the nanoTOF inlet transmission efficiency with electrospray generated tetra-alkyl ammonium halide clusters, size segregated by the Cluster Calibration Unit (Z to mobility equiv. diam.: 0.69 cm²/Vs = 1.73 nm; 0.72 cm²/Vs = 1.70 nm; 0.92 cm²/Vs = 1.50 nm; 0.96 cm²/Vs = 1.46 nm; 1.41 cm²/Vs = 1.21 nm).
In this figure, five individual AMC mobility scans, each of one cluster species, are shown. The AMC voltage is scanned from about 2000 V down to 0 V. For a cluster with a certain electrical mobility, the scan of the AMC from high to low voltage increases the transmission efficiency of the ion cluster over the potential barrier. Below a certain voltage, all clusters are allowed to pass. The slope of the resulting transmission efficiency curve determines the resolution power of the AMC with respect to the electrical mobility. The comparison of the final plateau value of the electrometer signal detected by EM2 downstream of the inlet and the signal reading from EM1 upstream enables the determination of the total size/mass dependent ion transmission efficiency of the nanoTOF inlet.

First experiments to test the performance of AMC and CID cell with the nanoTOF inlet coupled to the high resolution TOF-MS were carried out with the setup shown in Figure 3. Here, a commercially available soft x-ray aerosol neutralizer (TSI, 3087) was used to generate ionic molecular clusters in ambient laboratory air.

![Figure 3. Schematic of the experimental setup for the first nanoTOF performance test with the inlet coupled to the time-of-flight mass spectrometer.](image)

The AMC voltage was scanned from 1200 V down to 0 V in steps of 100 V (upper panel in Figure 4). Each AMC voltage step is associated with a critical mobility, allowing only clusters with mobilities lower than this critical mobility to enter the CID cell. To study the stability and fragmentation of the ambient ionic molecular clusters, the E/N inside the CID cell was changed in steps of 60 V from 0 V to 180 V (lower panel in Figure 4).

![Figure 4. Exemplary results of an AMC scan with four different CID-settings (steps from 0 V to 60, 120 and 180 V) for ions generated with a soft x-ray charger in ambient air (see text for details).](image)
Starting at high voltage, all clusters are blocked to further enter the instrument (left-hand side of Figure 4). With decreasing voltage, first the clusters with the lowest electrical mobilities are able to pass the AMC potential barrier. With each of the decreasing voltage steps, indicated by the broad coloured bands, clusters of higher and higher mobilities are transferred to the mass spectrometer. Within each AMC voltage step, the voltage controlling the cluster fragmentation in the CID cell is varied in four steps, indicated by the narrow stripe pattern within the broad bands of constant AMC voltage. The different colouring of the various bands represents different mass-to-charge distributions of the detected clusters.

CONCLUSIONS

In two different experiments the inlet of the new nanoTOF was characterized and the performance of its key features – AMC and CID – was tested. With the first set of experiments, a typical overall ion transmission efficiency of 50% was found for all studied tetra alkyl ammonium halide clusters. The resolution power of the AMC was determined to be in the range of R=3-4 for the current configuration of the inlet. Further optimization of the inlet is planned to significantly improve this value. The performance tests of AMC and CID using ambient ions generated by a soft X-ray aerosol neutralizer as shown in Figure 4 demonstrate that the mass-to-charge distribution of atmospheric ions is strongly dependent on the soft/hardness of the transmission from ambient pressure to vacuum. Further analysis of the so far obtained data will give deeper insights in the stability and fragmentation patterns of atmospheric ions during the transition from ambient pressure to the high vacuum.

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REFERENCES

Graus, M. et al. (2010), High Resolution PTR-TOF: Quantification and Formula Confirmation of VOC in Real Time, American Society for Mass Spectrometry 2010, 21, 1037–1044;
Junninen, H. et al. (2010), A high-resolution mass spectrometer to measure atmospheric ion composition, AMT, 3, 1039-1053;
Kirkby, J. et al. (2016), Ion-induced nucleation of pure biogenic particles, Nature, 533, 521-526;
Schobesberger, S. et al. (2013), Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules, P. Natl. Acad. Sci. 110, 43, 17223–17228;
EXPERIMENTAL INVESTIGATION OF AEROSOL PARTICLE COMPOSITION AND GROWTH RATES

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Keywords: nanoparticles, CPC battery, new particle formation.

INTRODUCTION

The chemical composition of naturally charged and neutral clusters can be determined using high resolution mass spectrometry. Clusters with masses up to roughly 1000 amu (=2 nm in mobility) can be chemically analysed with high resolution. The limitations of the high-resolution mass spectrometry comprise the selective charging (mostly nitrate ions are used as reagent, Jokinen et al., 2012), the limited upper size range and the quantification of the measurements. When studying new particle formation phenomena, the chemical composition and the formation rates of aerosol particles between 1.5 and 3 nm are crucial (Kulmala et al., 2014). Even though smaller clusters can exist, the relevance is determined by whether those clusters grow to larger sizes or not. Here we present a simple method to determine aerosol particle chemical composition and their growth rates. The instrument design is aimed at bridging the size gap between high resolution mass spectrometry and other mass spectrometers which are used for quantifying the chemical composition of aerosol particles starting from around 5 nm in mobility diameter.

METHODS

In this work, we present a measurement technique to indirectly determine the particle composition for the size range between 2 to 10 nm. The setup is shown in Figure 1. The particle growth rates can also be measured directly. The instrument consists of at least three different ultrafine CPCs, each using a different working fluid. The liquids used are water, butanol and DEG. The CPCs used in the CPC battery are tuned to the smallest sizes possible without generating homogeneous nucleation background in the instrument itself following a similar procedure as in Kuang et al., 2012. A similar device has been used already previously, showing that the hygroscopicity of the aerosol particles can be resolved (Kulmala et al., 2007). Upstream of the CPC battery, a Differential Mobility Analyser (DMA) will be used. Using a DMA has two advantages. First, the particle growth rates can be determined. Second, as the diameters are fixed at any given time during the measurement cycle, the detected signal in each CPC can be attributed to the interaction between the aerosol particle and the condensing liquid. This together with the results from the characterization in the laboratory allows for indirect determination of the chemical composition of the aerosol particles.

Various studies have shown that the activation efficiency of an ultrafine CPC strongly depends on the interaction between the condensing liquid and the chemistry of the aerosol particles that are measured (Iida et al., 2009). The results in Kangaslouma et al., 2014, showed that salt like aerosol particles are activated easier with the water based CPC compared to the butanol based CPC. The opposite was true for the other aerosol particle types (e.g. limonene ozonolysis products). By carefully characterizing the CPCs in the laboratory using different aerosol particle types, their response with respect to aerosol particle
composition is explored. This data will be used for inferring the chemical composition of the aerosol particles when the instrument is deployed for field measurements.

Figure 1. Experimental setup of the nano CPC battery. The electrometer will be used for the characterization measurements in the laboratory.

FIELD MEASUREMENTS

We will present preliminary results from the characterization of the instrument in the laboratory. The instrument will be deployed at the Hyytiälä field station during spring 2017. In addition to the data retrieved from the nano-CPC battery, the Hyytiälä station also provides other sub-3 nm aerosol particle size distribution and total concentration data. Mass spectrometer data for the smallest clusters is also available there, which allows to follow the nucleation and growth of the aerosol particles starting from the smallest clusters to larger (>10nm) sizes. In addition to that, comprehensive measurements of various trace gases, such as SO₂, O₃ and NOₓ are available which support the data that we will gather and help to understand better the processes attributed to the new particle formation.

ACKNOWLEDGEMENTS

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REFERENCES


CHARACTERISATION OF THE EFFECTS CAUSED BY SAMPLE AIR HUMIDITY TO THE PERFORMANCE OF A DIETHYLENE GLYCOL BASED PARTICLE SIZE MAGNIFIER

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Keywords: CPC, NUCLEATION, DIETHYLENE GLYCOL.

INTRODUCTION

The ability to measure small aerosol particles in the size range 1-2 nm in mobility diameter is important, e.g. for gaining better understanding of atmospheric nucleation and determining nucleation and growth rates for newly formed particles. Instruments capable for measuring electrically neutral clusters smaller than 2 nm have been developed recently and utilized in laboratory and ambient conditions (i.e. Manninen et al. 2010; Kirkby et al. 2011; Kulmala et al. 2013). Careful calibration of these instruments is crucial for getting comparable results for particle concentrations and nucleation and growth rates. To achieve more reliable calibration one needs to further investigate the uncertainties related to the measured concentrations. It has been shown in previous studies that in addition of particle's size and charging state, the chemical composition and also the relative humidity of the aerosol can change the instrument's cut-off diameter (Kangaslouma et al. 2013; Kangaslouma et al. 2016b). Characterizing these effects is especially important for the interpretation of field measurements during which the ambient temperature and relative humidity can change considerably.

METHODS

The Airmodus Particle Size Magnifier (PSM) is a continuous flow particle size magnifier in which heated and saturated flow is mixed turbulently to the sample air. The mixed flow is then cooled in the growth section where supersaturation of diethylene glycol is achieved (Vanhanen et al. 2011). In this study we determined thoroughly the effects that air humidity has on the performance of this diethylene glycol based particle size magnifier. Detection efficiency of the PSM was tested in the laboratory at various sample flow humidity conditions using also different operation temperatures. In the measurement setup a tube furnace or an electrospray was used for producing the test particles while a Herrmann-type high-resolution DMA (Herrmann 2000; Kangaslouma et al. 2016a) in closed loop was used to size classify the produced particles. Closed loop was used to get better control of the conditions of the sheath air. Particles were generated to a flow of dry gas taken from pressurized air and nitrogen. The sample air was humidified by mixing filtered humidified air to the sample flow downstream of the DMA. The humidity level of the sample air was set by controlling the temperature inside a water filled humidifier and measured with a dewpoint meter (EdgeTech DewMaster) placed parallel to the PSM. An electrometer (TSI 3068B) was also placed parallel to the PSM and was used as the concentration reference device.

During the measurements particles were produced from ammonium sulfate and tetra-alkyl ammonium halides (Ude and Fernandez de la Mora 2005) to study the humidity effect for particles of different size and chemical composition. The PSM was run in fixed saturator flow mode and in scanning mode where the saturation ratio is changed periodically. Detection efficiency was determined as the fraction of the concentrations measured with the PSM and the reference instrument \( N_{psm}/N_{electrometer} \).
RESULTS

We observed that the amount of water in the sample air has a noticeable effect to the diethylene-based instrument’s ability to detect small particles. We saw an enhancement in the detection efficiency, which has been also reported in earlier studies (Iida et al. 2009; Kangasluoma et al. 2013). At higher humidity we could detect smaller particles with the same operating temperatures and flow rates than in dry conditions. In one experiment the cut-off diameter (diameter with 50% detection efficiency) was set approximately to 2 nm in dry air by tuning the operation temperatures. After increasing sample air humidity to 35 % at room temperature, the cut-off diameter decreased from around 2 nanometer to less than 1.4 nanometer. The experiment was conducted with ammonium sulfate particles produced with tube furnace. The results are shown in the Figure 1.

![Graph](image)

Figure 1. The cut-off diameter of the PSM against the relative humidity for ammonium sulfate particles. The cut-off diameter decreases from around 2 nm to 1.4 nm when the sample air humidity increases from close to 0 % to 35 %.

In scanning mode the flow rate through the PSM’s saturator is changed periodically. Larger saturator flow rate means more diethylene glycol vapor and higher supersaturation in the growth section. For this reason, the detection efficiency increases with increasing saturator flow rate for specific sized particles. When measuring electrospayed tetra-heptyl ammonium bromide monomer (1.47 nm in mobility diameter) we got several different saturator flow -detection efficiency curves depending on the sample air humidity. The graphs, all measured with the same PSM settings, are shown in the Figure 2. If there was no change caused by humidity one should get only a one detection efficiency curve. Thus we can say that THAB monomer particles can be activated with smaller amounts of diethylene glycol vapor in high humidity conditions than in dry air.
Figure 2. Measured detection efficiency for the THAB-momer with 1.47 nm mobility diameter against the saturator flow in different humidities. Horizontal axis is flow rate through the saturator and different colors are used to distinguish different humidity values. Operating temperatures was kept the same.

CONCLUSIONS

We have shown in this study that water has a noticeable enhancing effect to the detection efficiency of the PSM using diethylene glycol as working fluid, and quantified this effect for various particle sizes and types. The difference to the activation flows, which are used in the calibration of the device, was measured for a wide variety of conditions. This difference in the activation of aerosol particles in the instrument should be further studied and also taken in to consideration when calibrating the device for different environments, and interpreting the data measured at different relative humidities. These measurements can possibly also be used to improve calibration and measurement routines in the future.

ACKNOWLEDGEMENTS

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REFERENCES


ON THE TEMPERATURE DEPENDENCE OF HETEROGENEOUS NUCLEATION OF N-BUTANOL VAPOR ON SILVER AND SODIUM CHLORIDE NANOPARTICLES

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Keywords: TEMPERATURE DEPENDENCE, HETEROGENEOUS NUCLEATION, N-BUTANOL, SILVER, SODIUM CHLORIDE.

INTRODUCTION

Commercial Condensation Particle Counters (CPCs) are mainly used to measure the number concentration of airborne particles (McMurry, 2000). Most ultrafine continuous flow CPCs use n-butanol as working fluid and have typical lower particle detection limits in the range between 2.5 and 10 nm (Stolzenburg and McMurry, 1991). Given the fact that n-butanol CPCs are operated at fixed temperatures, the performance towards the detection of even smaller particles may be optimized by choosing appropriate temperature settings.

Until now the temperature dependence of heterogeneous nucleation of n-butanol vapor on nano-particles in a size-range down to 2.5 nm was not investigated. A topic, however, that is worth examining since it gives information on the saturation ratio which is needed to activate particles in this size range. Results of earlier experiments with water vapor nucleating on silver particles have shown a theoretically unpredictable maximum in the onset saturation ratio as a function of temperature (Kupc et al., 2013). Further studies on the nucleation of n-propanol on sodium chloride particles in the temperature range from 262K to 287K indicate a reversed trend of the onset saturation ratio compared to the Kelvin equation (Schobesberger et al., 2010). Due to the close chemical similarity of n-propanol and n-butanol, and the common use of n-butanol as a working fluid in commercial CPCs, the temperature dependence of heterogeneous nucleation of n-butanol on Ag and NaCl particles is investigated in this study.

METHODS

Here we report measurements of heterogeneous nucleation of n-butanol at nucleation temperatures ranging from 269 K to 289 K. To this end, we generated monodisperse NaCl and Ag particles using a tube furnace particle generator (Scheibel and Porstendörfer, 1983) in combination with a Vienna type differential mobility analyzer for size selection. Subsequently, particles were mixed with n-butanol vapor and led into the expansion chamber of the Size Analyzing Nuclei Counter (SANC) (Wagner et al., 2003). N-butanol vapor was added to the system by controlled injection from a syringe pump, followed by quantitative evaporation of the liquid beam in a heating unit (Winkler et al., 2008). Thereby, a well-defined and nearly saturated binary vapor-air mixture together with size selected, neutralized monodisperse seed particles from the DMA were passed into the temperature controlled expansion chamber of the SANC. A schematic diagram showing the experimental setup is illustrated in figure 1. Vapor supersaturation was achieved by adiabatic expansion and the number concentration of droplets nucleated on the seeds was measured with the Constant Angle Mie Scattering (CAMS) method (Wagner, 1985). Therewith the radius and the number concentration of the growing droplets can be determined simultaneously. By varying the chamber temperature and the pressure drop in the expansion chamber, different nucleation conditions were analyzed. The nucleation or activation probabilities (shown in figure 2) using the SANC/CAMS method can be expressed as:
\[ p = \frac{N_{\text{activated}}}{N_{\text{total}}} = 1 - e^{-j t}. \]

Here, \( j \) is the heterogeneous nucleation rate and \( t \) is the time for activation. We define the onset conditions as the saturation ratio \( S_0 \) when the nucleation probability reaches the value \( P = 0.5 \).

The nucleation probability \( P(S) \) at \( S_0 \) has the form of a cumulative Gumbel distribution (Winkler et al., 2016)

\[ P(S) = 1 - \exp\left[ -\exp\left( \frac{\ln(S/S_0)}{2} + (n^* + 1)(\ln S - \ln S_0) \right) \right]. \]

By applying this form of distribution as a two-parameter fit function to the experimental data the parameters \( n^* \) (number of molecules in the critical cluster) and \( S_0 \) can be evaluated. The resulting onset saturation ratio depending on the nucleation temperature can be compared to Kelvin prediction. As a result, heterogeneous nucleation of n-butanol vapor on NaCl and Ag aerosol particles shows different behavior depending on the nucleation temperature. An inverse temperature trend for NaCl seeds was identified when compared to the Kelvin prediction. No such trend could be found for silver nano-particles. In addition to the SANC measurements, the counting efficiency of an ultrafine continuous flow CPC (Model UCPC 3776, TSI Inc., Minneapolis, USA), whose temperature settings were changed over a range of 20 degrees, was measured. The particles were size selected with a Vienna type UDMA (Steiner et al., 2010) and the counting efficiency was determined relative to a Faraday cup electrometer operated in parallel as shown in figure 3.

![Schematic diagram for the experimental setup of the SANC.](image)

**Figure 1.** Schematic diagram for the experimental setup of the SANC.

At the standard temperature settings of the UCPC 3776 the measured counting efficiencies of Ag particles agree nicely with the data published in the manual. However, for the same temperature settings the activation behavior of NaCl particles looks considerably different. The cut-off diameter has moved to a larger size and the slope is not as steep as for Ag particles. These findings are consistent with data reported in the literature (Ankilov et al., 2002; Hermann et al., 2007) and would conventionally be explained by a composition
dependent CPC response. Therefore it is notable that by reducing the nucleation temperature by only a few K, we find counting efficiencies of the NaCl particles exceeding those for Ag particles. The heterogeneous nucleation of butanol on NaCl seed particles thus indicates a clear dependence on nucleation temperature.

![Figure 2](image)

**Figure 2.** Heterogeneous nucleation of n-butanol on silver seeds at different nucleation temperatures. In this case, lower nucleation temperature coincides with higher saturation ratios needed for particle activation.

**CONCLUSION**

We have measured the onset saturation ratio of n-butanol in dependence of nucleation temperature with the SANC and determined the cut-off diameter at variable condenser temperature, but constant ΔT between Saturator and Condenser, for a commercial n-butanol CPC. NaCl and Ag seeds in the size range from 2.5 to 9.0 nm have been used as condensation nuclei. An inverse temperature dependence of heterogeneous nucleation of n-butanol on sodium chloride particles was found, resulting in a lower cut-off diameter for NaCl particles at reduced temperatures. Accordingly, by lowering the condenser temperature and hence nucleation temperature of a butanol CPC the counting efficiency can be increased significantly for both NaCl and Ag seeds, with a stronger response for NaCl particles. This finding is of immediate relevance for nanoparticle detection in CPCs and raises questions on the fundamental mechanisms leading to this behavior.
Figure 3. Schematic diagram of the experimental setup for counting efficiency measurements.

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REFERENCES


Alternating Sign Preference in Ion-induced Nucleation

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Keywords: HETEROGENEOUS NUCLEATION, ATOMIC CLUSTERS, CHARGE EFFECT, CONDENSATION PARTICLE COUNTER.

INTRODUCTION

Ion-induced nucleation is an atmospheric mechanism with potentially important environmental implications. Atmospheric ions can form efficient nuclei on which inorganic and organic vapors can condense, thereby yielding high concentrations of newly-formed airborne nanoparticles that can affect human health (Pöschl, 2005). Newly formed particles by ion-induced nucleation can further grow to optically active sizes by further condensation and/or coagulation, and thus affect the visibility of the atmosphere (Kulmala et al. 2000), as well as the atmosphere of the Earth in a direct manner (Haywood and Boucher, 2000). What is more, atmospheric ions can form perfect cloud condensation nuclei (CCN) when exposed to high water vapor supersaturations, which in turn can have indirect effect on the Earth’s climate (Merikanto et al. 2009).

Observations since the historical Wilson cloud chamber experiments (Wilson, 1897) have shown that negatively charged ions are more efficient condensation nuclei compared to positive ions; a phenomenon which is commonly referred to as the sign preference paradigm in the literature (Kangashuoma et al.,2016). Despite the vast amount of experimental evidence corroborating this paradigm, however, the high variability in size and composition of the ions observed in the atmosphere makes understanding of this phenomenon far from complete. This is also reflected by a number of theoretical studies, which in some cases report contradicting results (Nadykto et al., 2006; Keasler et al., 2012; Kathmann et al., 2005).

In this paper we describe an experimental apparatus that can be used to investigate the dependence of ion-induced nucleation on the polarity of the seed ions. More specifically, we use spark ablation to produce pure metal ions (Ag), having sizes that range from that of a single ion to ionic clusters of a few tens of atoms, and investigate their ability to act as condensation nuclei. Using n-butanol as a working fluid, we show that the sign preference paradigm holds true when the size of the ions is larger that 1.3 nm. Surprisingly, however, this sign preference shifts, and positive ions appear to be more efficient condensation nuclei. This observation can be explained by crude calculations using the Thompson model and theoretical considerations of the structure of the ions and the condensing vapor.
METHODOLOGY

Figure 1 shows the experimental setup used to investigate the effect of the size and polarity of ions on ion-induced nucleation. The ions, or more precisely the charged atomic clusters, used in the experiments were generated by a spark discharge generation (SDG) using high purity Ag electrodes (Goodfellow Inc., USA). Details of the generation method of the charged atomic clusters by the SDG are provided in a previous publication by our group (Maisser et al., 2015). In brief, material is evaporated from two electrodes by electrical discharges, and the resulting vapors are subsequently diluted and cooled by a gas flow. The size of the charged clusters and/or particles depends on the energy of the electrical discharge, which can be controlled by the gap between the two electrode (gas breakdown voltage) and by the electrical circuit controlling the spark energy and frequency. For the generation of atomic clusters the energy for the electrical discharge is kept small and the dilution flow high. To avoid contamination of the generated clusters the dilution gas was purified by passing it through a water and oxygen trap as shown in Figure 1.

The clusters were classified and size-selected by a half-mini DMA (Fernandez de la Mora and Kozlowski, 2013) to produce near-monodisperse clusters. The ability of the resulting Ag clusters to induce heterogeneous nucleation was determined by measuring their number concentration with a commercial ultrafine condensation particle counter (CPC; TSI Model 3025) in parallel with a custom-made and calibrated aerosol electrometer (AEM). The AEM measured the total concentration of classified singly charged atomic clusters downstream the DMA, while the CPC gave a signal that was proportional to that concentration, and their activation probability that depends on their size and polarity. The ratio of the concentrations measured by the CPC and the AEM gives the detection efficiency of the CPC, which is proportional to the activation probability of the monodisperse ions.

![Figure 1. Schematic layout of the experimental setup used for measuring the activation probability of silver atomic clusters. Key: AEM, Aerosol Electrometer; CPC, Condensation Particle Counter.](image)

The CPC was operated at increased supersaturation inside the growth tube compared to its default settings to enable the detection of sub-1-nm sized particles (Kuang et al., 2011). It was ensured that the homogeneous nucleation level was below 5 #/cc for a low noise to signal ratio.

RESULTS AND DISCUSSION

The experimental results show that ionic clusters with a mobility equivalent diameter of 1.3 nm (corresponding to ions having inverse mobility of 0.8 Vs/cm²) or larger, are detected more efficiently compared to their positively charged counterparts of equal size (cf. Figure 2). However, as the particle size decreases further, the trend shifts and positively charged cluster ions are detected with a higher efficiency compared to negatively charged clusters.
Figure 2. Measured detection efficiency of positively and negatively charged silver atomic clusters versus inverse electrical mobility.

A possible qualitative explanation for this trend is that charged atomic clusters with the same number of atoms have a smaller size when they are positively charged than when they are negatively charged as a result of the difference in the number of electrons. This trend that decreasing size of the ion is beneficial for the nucleation process for very small ions is suggested by the classical ion-induced heterogeneous nucleation theory, described by the Kelvin-Thomson model, which can be expressed as follows:

\[ G = kT \ln \left( \frac{p}{p_{sat}} \right) + \sigma 4\pi \left( r_n^2 - r_{n-1}^2 \right) \left( \frac{q^2}{8\pi \varepsilon_0} \right) \left( 1 - \frac{1}{\varepsilon_0} \right) \left( 1 - \frac{1}{\varepsilon_0} \right). \]  

Here \( \Delta G \) is the change in the Gibbs free energy, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( p \) is the partial vapor pressure, \( p_{sat} \) is the saturation vapor pressure, \( \sigma \) is the surface tension, \( r_n \) is the radius of an ion with \( n \) vapor molecules (\( n \)-mer), \( q \) is the number of charges, \( e \) is the elementary charge, \( \varepsilon_0 \) is the vacuum permittivity, and \( \varepsilon_0 \) is the relative permittivity of the bulk liquid. As indicated by this model, the probability for an already attached vapor molecule to evaporate is reduced by the dipole interaction of the polar vapor molecule with the ion. This effect scales with the inverse of the ion size, and thus is stronger for very small ions.

In addition, the structure of the n-butanol molecule can also provide a possible quantitative explanation for a positive charge effect up to a certain size. The permanent dipole moment of the n-butanol molecule would orient itself with the oxygen molecule facing the charge and thus would assemble the first layer of molecules around the ion in a star-shaped structure. In contrast, for the negatively charged ions the chain shaped n-butanol vapor molecules would orient with the side toward the ion. This means that for a monolayer a larger number of ions would be needed for positively charged ions, than for negatively charged ions. In addition, the star-shaped structure of the vapor molecules around a positive ion leads to a stronger increase of the surface of the pre-nucleation cluster ion, compared to negatively charged ions and thus makes further activation more likely.

Another possible explanation would be that the effect of different activation efficiencies in the CPC is a result of impurities of the charged Ag clusters. These could be e.g. oxygen or also water molecules sticking to the clusters and altering their chemistry (Kangaslouma et al., 2016). Because of significant efforts in
avoiding contaminations in the generation procedure of the clusters by using high purity bottled gas and additional columns to remove both water and oxygen traces it is expected that these impurities would be minor and thus not fully explain the observed effect.

CONCLUSIONS

In this study, we investigated the effect of charge polarity on the activation probability of atomic clusters of the same chemical composition.

The results show that the negatively charged ions are activated with higher probability for ions larger than about 1.3 nm, while at smaller sizes we see that this trend switches. This cross-over, to our understanding, is the point of a regime switching from the nucleation process being dominated mostly by the surface tension of the vapor-coated cluster (Kelvin effect) to a regime where the charge (Thomson effect) becomes significant due to the small size of the ion and thus strong ion dipole interaction. In this regime not only the chemistry and physical structure of the ions becomes important but also the orientation of the vapor molecule around the ion, especially for the first layer of molecules.

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REFERENCES


ON SELECTED SOURCES OF UNCERTAINTY IN THE SUB-3 NM PARTICLE CONCENTRATION MEASUREMENT

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Keywords: uncertainty, cluster, instrumentation

INTRODUCTION

Recently, an interest to understand gas-to-particle conversion (often called as new particle formation, NPF) and sub-3 nm particle dynamics in various fields of aerosol science has grown tremendously. Direct measurement of NPF includes chemical characterization of the nucleating species, often via mass spectrometric methods, and measurement of size resolved particle concentrations to infer particle nucleation and growth rates.

Size resolved particle concentrations can be measured by two independent methods. In the first method, particles are first brought to charge equilibrium usually with a radioactive source. The charged particles are mobility classified with a differential mobility analyzer (DMA) and finally counted by a condensation particle counter (CPC) (DMA-CPC method). The second method is to alter supersaturation inside a CPC to vary the CPC d50 diameter (diameter at which the CPC detects 50% of the sampled particles). By varying the d50, size resolved particle concentration can be inferred from the concentration differences measured at different d50s (PSM method).

With the current state-of-the-art instrumentation, both methods include various sources of uncertainty, which have not been assessed previously. These sources include steep particle size distributions as a function of the particle size, the width of the DMA transfer function, a non-ideal CPC d50 curve and its dependency on the particle chemical composition and charging state, and CPC counting statistics. In the four case studies, we assess the counting statistics of the current state-of-the-art DMA-CPC instrument (Jiang et al., 2011), and especially the effect of steep size distributions on the counted particle concentrations when the CPC d50 is not well known.

METHODS

The study presents numerical calculations on CPCs and DMA-CPCs sampling three different particle size distributions. We parametrized d50 curves of three different CPCs, Airmodas A11, TSI 3777 and ADI vWCPC according to Vanhanen et al. (2011) and Kangashuoma et al. (2017), and one ideal CPC with d50 at 1.5 nm. These CPCs were used to sample three different particle size distributions (SD) with and without the TSI nano DMA in between.

A CPC directly monitoring a SD detects concentration according to:

$$C_{tot} = \sum C_{SD}(dp) \times \eta_{CPC}(dp)$$

(2)

where $C_{sd}(dp)$ is the size dependent concentration of a particle size distribution, $\eta_{CPC}(dp)$ is the d50 curve for a given CPC, $C_{tot}$ the detected concentration.

In the DMA-CPC method the DMA transfer function was calculated according to Stolzenburg and McMurry (2008). The TSI nano DMA was used as the DMA with aerosol flow rate of 2 lpm and sheath flow rate of 20 lpm. A concentration detected by a DMA-CPC system monitoring a SD was calculated as:

$$C_{det}(dp) = C_{SD}(dp) \times \eta_{CPC}(dp) \times \Omega_{dp}$$

(3)
where $\Omega_{dp}$ is the DMA transfer function when the DMA is set to sample a selected particle size and $C_{\text{det}}(dp)$ the concentration detected at a given particle size. From $C_{\text{det}}(dp)$ the inverted SD was calculated as:

$$C_{\text{inv}}(dp) = \frac{C_{\text{det}}(dp)}{\eta_{\text{CPC,dp}} \cdot \int \Omega_{dp} \cdot \eta_{dp} \cdot A}$$  \hspace{1cm} (4)

where $\eta_{\text{CPC,dp}}$ is the detection efficiency of a CPC at a given diameter, $\int \Omega_{dp}$ is the surface area of the transfer function, $C_{\text{inv}}(dp)$ is the inverted concentration and $A$ is the d50 curve plateau value. In the inversion $\eta_{\text{CPC,dp}}$ and $\Omega_{dp}$ are single values, assuming that the size distribution does not change significantly over the size range of the DMA $\Omega$, or where the d50 curve goes from 0 to plateau value. On the contrary, $C_{\text{det}}(dp)$ includes the d50 curve shape and DMA $\Omega$ shape. One of the purposes of this study is to examine the validity of this assumption. the PSM method was analysed.

Uncertainty in the d50 was included so that ±0.5 nm was inserted to the d50 curve of the CPCs, and the detected concentrations with the “wrong” d50 were compared to the “real” particle concentrations in the distribution.

RESULTS AND CONCLUSIONS

Figures 1 and 2 present one example case in which the DMA-CPC system was sampling one of the size distributions. Even with the well-known CPC d50, the inversion and instrumental non-idealities introduce error to the inverted concentration (Figure 1 lower panel). If ±0.5 nm uncertainty is inserted to the CPC d50, the error in the inverted concentration span from -100% to >1000% depending on the sampled particle size and uncertainty of the d50.

Our results show that sampling steep size distributions can cause errors in the inverted concentrations due to non-ideal instrumentation. These errors are further magnified if the CPC d50 is not well-known. However, the exact magnitude of the uncertainties cannot be easily quantified due to its dependence on the sampled particle size distribution.

Further instrumental development is still required to perform more reliable particle concentration measurements in the sub-3 nm size range. DMAs with higher mobility classification resolution, CPCs with steeper d50s and smaller d50 dependency on the particle chemical composition will reduce the uncertainties significantly.
Figure 1. Inverted concentrations, and the ratios of inverted concentrations to the initial size distribution as a function of size.

Figure 2. Same as Figure 1 lower panel, but ±0.5 nm uncertainty in the CPC d50s.
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REFERENCES


SESSION 15:
PARTICLE PHASE CHANGE

Mark Holden: Investigating active sites for immersion mode ice nucleation on alkali feldspars

Miklós Szakáll: Retention of organic and inorganic substances during the phase change induced by rimeing

Manish Shrivastava: Viscous secondary organic aerosols elevate global long-range transport and lung-cancer risk
INVESTIGATING ACTIVE SITES FOR IMMERSION MODE ICE NUCLEATION ON ALKALI FELDSPARS

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Keywords: ICE, NUCLEATION, ACTIVE-SITES, IMMERSION, FELDSPAR.

INTRODUCTION

In the absence of foreign particles, water in clouds can supercool to below -33 °C. Particles immersed in cloud droplets are able to catalyze ice formation at warmer temperatures; the exact freezing temperature is related to the efficiency of the ice nucleating particle (INP). In mixed-phase clouds, mineral dusts are an important class of INP (Hoose and Möhler 2012; Murray et al. 2012). In particular, feldspars have been identified as the most important component, owing to their ability to catalyze freezing at warmer temperatures than other mineral phases (Atkinson et al. 2013). Of the feldspars, those containing $K^+$ and $Na^+$ are known as alkali feldspars, whilst those containing $Na^+$ and $Ca^{2+}$ are known as plagioclase feldspars. Certain alkali feldspars have been shown to nucleate ice at warmer temperatures than plagioclase feldspars (Harrison et al. 2016). However, the reason that some alkali feldspars are such efficient INPs in the immersion mode is not fully understood.

In deposition mode experiments on alkali feldspars, ice nucleation was shown to originate in cracks in the surface. The ice crystals that grew at higher temperatures were oriented. Through computational modelling, it was shown that this orientation related to favourable nucleation on the (100) face (Kiselev et al. 2016). For immersion mode nucleation, Whale et al. have found that ‘perthitic microtextures’ in alkali feldspars give rise to their superior nucleating efficiency compared to plagioclase feldspars (Whale et al. 2017). These ‘microtextures’ are features and topographies that result from separation of the $K^+$ and $Na^+$ into discrete regions, and include the cracks from which ice nucleated in the deposition mode experiments of Kiselev et al. (Parsons et al. 2015). Alkali feldspars that do not contain these ‘perthitic microtextures’ nucleate ice at colder temperatures, similar to plagioclase feldspars. Therefore, it may be that the topographies formed during alkali feldspar cation separation, revealing the (100) face, are sites for nucleation in immersion mode too.

Whilst nucleation sites related to a specific crystal face have been proposed, typical immersion mode experiments are not able to investigate individual crystal faces (Slater et al. 2015). This is because samples are ground or milled, meaning that a mixture of crystal faces are present on each particle and in each water droplet. Here, we use flat sheets of alkali feldspars to investigate immersion freezing on specific crystal faces. We investigate freezing efficiencies on the two cleavage planes, the (010) and (001), and compare these to ground, immersed particles. Using freeze thaw experiments, we characterize the distribution of active sites on the surface. We find that the ice nucleating efficiencies on the (010) and (001) faces of both feldspars investigated are the same as those for the ground, immersed particles. We also find that the freezing efficiency across the feldspar surface is not uniform, meaning that there are specific locations, or sites, on the surface that control the freezing temperature.
METHODS

Two alkali feldspars were selected for this study; one containing ‘perthitic mictotextures’, and one in which the cations were not separated, known as ‘microtexturally pristine’ (Parsons et al., 2015; Whale et al., 2017). Petrographic thin sections of the alkali feldspars were prepared. This involved cleaving the samples along the (010) and (001) faces and mounting them on glass slides. Through sequential polishing, the thickness of feldspar was reduced to 30 µm. The final polish was performed with 0.25 µm diamond powder. Arrays of MilliQ water were pipetted onto the surface of the thin sections, and freezing experiments were performed on the µL-NIPI, described by Whale et al. (2015). The thin sections were cooled at a constant 1 Kmin⁻¹ ramp rate, recording the temperatures of freezing events. The data obtained here were compared to gravimetric dilutions of suspensions of ground feldspar particles. Comparisons between the two methods were performed by converting the fraction frozen to active site density, n(T), using:

\[ n(T) / N = 1 - \exp(-n(T) A) \]  \hspace{1cm} (1)

where \( n(T) \) is the number of droplets frozen at temperature \( T \), \( N \) is the total number of droplets in the experiment and \( A \) is the surface area per droplet (Connolly et al. 2009). The surface area per droplet, \( A \), was calculated using the BET surface area for immersed particles, whilst the contact area was used for thin sections.

Freeze-thaw experiments were performed on thin sections to compare the freezing temperatures of individual droplets, in a similar manner to Vali (2008). In these experiments, the feldspar was cooled at 1 Kmin⁻¹ until all droplets were frozen. The droplets were then brought to 278 K, and then they were re-frozen at 1 Kmin⁻¹. The freezing temperatures of each droplet were recorded and compared between the individual runs. Several cycles were performed for both feldspars.

RESULTS

Figure 1. Experimental results for (a-d) perthitic and (e-h) non-perthitic alkali feldspars. (a,e) cross-polarised light microscopy revealing the microtexture of the perthitic LD3 microcline in (a), and the lack of microtexture in Eifel sanidine (e); (b,f) EDX mapping showing the locations of K⁺ (green) and Na⁺ (gold) in the feldspars tested. In (b), the two are separated into discrete ‘exsolved’ regions, in (f) the cations are mixed in a ‘solid solution’; (c,g) Plot of active site density, \( n(T) \), comparing freezing temperatures on thin sections of selected crystal orientations and ground immersed particles for (c) LD3 microcline and (g) Eifel sanidine; (d,h) correlation plots showing the freezing temperatures of individual droplets in a freeze thaw experiment, selecting cycles 1 and 2, for (d) LD3 microcline and (h) Eifel sanidine.
In Figure 1, the results from immersion mode experiments are shown, alongside micrographs characterizing the feldspars investigated. Figures 1a–b, and Figures 1e–f, show the difference between a perthitic and non-perthitic feldspar. In the light microscope images, the striking difference between a feldspar containing microtexture and one without is shown. The EDX maps show that for LD3 microcline, the cations have separated into discrete regions, whereas for Eifel sandstone they are mixed. This difference in microtexture was shown by Whale et al. (2017) to be important in determining ice nucleation efficiencies. In Figure 1c and 1g, active site densities, \( n_a(T) \), are shown for these experiments. For feldspars both with and without microtextures, there is good agreement between the active site densities of ground, immersed particles and water droplets on a specific crystal face of feldspar. This demonstrates that the sites that control freezing on ground particles are also present in similar concentrations on both crystal faces tested. We also note that these results demonstrate that the active-site densities measured for feldspar particles in ‘wet-suspension’ methods are not affected by aggregation, as suggested by Emerson et al. (2015).

The results of freeze-thaw experiments are shown in Figures 1d and 1h. These show that droplets in specific regions always freeze at higher temperatures than droplets in other regions. This means that there is a distribution of sites across the surface, and that this distribution is of first-order importance in determining the temperature at which a water droplet will freeze. This is in agreement with the freeze-thaw experiments on immersed feldspars by Peckhaus et al. (2016). The reason that some areas consistently nucleate ice at warmer temperatures than others could be related to the amount of \( (100) \) face exposed in each droplet, since this face is known to nucleate ice well in deposition mode (Kiselev et al. 2016). However, this would mean that concentrations of the \( (100) \) face present under different droplets would have to vary significantly, which seems unlikely given the number of cracks covered by each mm diameter droplet. Instead, we propose that other factors, in concert with the templating of the \( (100) \) face, affect the nucleating efficiency of a particular site. These factors could be related to the topographies introduced through the exsolution process, which may create geometries that stabilize the ice critical nucleus (Whale et al. 2017).

CONCLUSIONS

We have investigated the immersion mode ice-nucleation efficiencies of two alkali feldspars; one with perthitic microtexture, and one without. By using petrographic thin sections, we have demonstrated that the two cleavage planes, (010) and (001), have similar ice active-site densities to ground, immersed particles. From freeze-thaw experiments on arrays of droplets, we demonstrate that the freezing temperature has a first-order dependence on the location of the droplet on the feldspar surface. This heterogeneous ice nucleating activity demonstrates that the bulk framework is not responsible for feldspar ice nucleation activity, but instead ice-nucleation active sites exist on feldspar surfaces.

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REFERENCES


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RETENTION OF ORGANIC AND INORGANIC SUBSTANCES DURING THE PHASE CHANGE INDUCED BY RIMING

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Keywords: riming, retention, mixed-phase clouds, phase change chemical processes.

INTRODUCTION

The largest precipitation particles in mixed phase clouds, graupel and hailstones, grow by accretion of small supercooled liquid cloud droplets. This microphysical process is the so-called riming, during which a phase transition from liquid to ice occurs as the supercooled droplets freeze onto the surface of the glaciated hydrometeor upon contact. Rimming is the most effective growth processes in mixed-phase clouds (Pruppacher and Klett, 2010). Furthermore, riming is also involved in the partitioning of volatile trace substances of the atmosphere. During the freezing process of the liquid droplets on the ice particles’ surface trace chemical substances dissolved in the liquid escape from the developing crystal structure. This partitioning is quantified by the retention coefficient defined as the ratio of the concentration of the substance in the aqueous phase prior to riming and the concentration of the substance in the ice phase after freezing. Unless scavenged by precipitation, these substances contained in the ice phase will be released back to the air by evaporation, e.g., at higher altitudes, if they are carried aloft in convective cloud systems. Thus, retention during riming plays an important role in the redistribution and transport of atmospheric trace substances which in turn may influence oxidation processes in the atmosphere. Nevertheless, retention is one of the main uncertainties in cloud resolving models which simulate the redistribution of trace substances by convective storms (e.g.: Barth et al., 2007a, Leriche et al., 2013, Bela et al., 2016). Further, the scavenging of trace substances and subsequent precipitation of them play a significant role in the global distribution and is an additional source of uncertainty related to the convection parameterizations in global models (Tost et al., 2010). The dependencies of the retention coefficient could be determined by systematically studying the ratio of the involved timescales for mass transport (aqueous phase, interfacial, gas phase) to the freezing time of the droplets (Stuart and Jacobson, 2003, 2004). On the one hand the retention coefficient was found to be highly dependent on chemical factors such as the effective Henry’s law constant accounting for solubility and dissociation. On the other hand physical factors such as temperature, ventilation, droplet size, and the liquid water content might significantly affect the retention coefficient (Stuart and Jacobson, 2003, 2004, 2006; von Blohn et al., 2011, 2013). Therefore, we present here the results of wind tunnel experiments carried out to investigate the retention coefficients of watersoluble inorganic and organic substances during this phase change under conditions close to the ones prevailing in the mixed phase zone of convective clouds.

METHODS

In the Mainz vertical wind tunnel atmospheric particles of different sizes can be freely suspended at their terminal velocities in a vertical air stream (Diehl et al., 2011). Two vacuum pumps are maintaining the continuous air flow through the tunnel. Wind tunnel speeds up to 40 m/s are possible so that hydrometeors of different sizes from a few micrometers up to several centimeters can be investigated. Thus, ventilation as well as heat and mass transfers concerning hydrometeors are similar to those in the real atmosphere. The wind tunnel air can be cooled down to -30 °C, which ensures the investigation of microphysical and chemical processes under mid to upper tropospheric conditions in mixed phase clouds. A cloud of supercooled
droplets containing a single chemical component to be investigated was produced upstream of the rime collector with the means of sprayers.

The conditions in the wind tunnel during the riming experiments correspond to those under which riming is most effective in the atmosphere (Pruppacher and Klett, 2010); that is, the temperature ranged from -16 to -7°C, the liquid water contents varied between 0.7 and 1.7 g/m³, and vertical wind speeds from 2 to 3 m/s depending on the rime collector type. The captively-floated ice particles had a constant diameter of 8 mm and the quasi-floated snowflakes had diameters between 8 and 12 mm. These conditions correspond to the dry growth regime, i.e. the surface temperature of the collectors were below 0°C during riming. The substances were investigated individually with liquid phase concentrations ranging from 30 to 100 μmol/l and pH values ranging from 3.3 to 5.3.

RESULTS AND DISCUSSION

Fig. 1 shows a representative example of the measurements. Depicted are the retention coefficients of sulfur dioxide as function of temperature. As indicated by the linear regression the parameterized retention coefficient shows a negative dependency of the temperature. We have experimentally confirmed in the present wind tunnel study that for most of the investigated substances the retention coefficient can properly be estimated by means of the effective Henry’s law constant. Thus, the retention coefficients of the substances increase with increasing solubility or – the other way around – they decrease with increasing volatility. Consequently, very soluble substances like hydrochloric acid and nitric acid show retention coefficients close to 1. In contrary, as predicted also by the timescale analysis of Stuart and Jacobson (2003, 2004), more volatile substances – such as sulfur dioxide, for instance – show low retention coefficients. The retention coefficients of such substances are also dependent on ambient temperature and ventilation, i.e. enhancement of mass and heat transfer due to flow around the collector (see Fig. 1). We found that the dependency on the effective Henry’s law constant can only be confirmed for substances for which aqueous phase processes occur quickly compared to mass transport processes. For substances which are limited by aqueous phase reactions, such as ammonia in the presence of CO₂ (Hannemann, 1995), and formaldehyde, the estimation of the retention coefficient by the effective Henry’s law constant fails. In these cases, one has to account for the appropriate timescales for aqueous phase reactions when describing retention. This becomes especially important during freezing of a ventilated spread cloud droplet of 10 μm (typical timescale of 1 ms) in radius. The mean values of the measured retention coefficients range from 0.2 for sulfur dioxide up to 1.0 for nitric acid and hydrochloric acid, respectively. These high values validate retention during riming as an efficient scavenging process for water-soluble trace substances. These findings were confirmed by the investigation of organic species such as formic acid, acetic acid, oxalic acid, and formaldehyde. From the whole dataset a reliable relationship between the retention coefficients and the effective Henry’s law constant was obtained.

In conclusion one can say that the derived parameterization can be applied for all substances whose aqueous phase reaction kinetics are fast compared to the involved mass transfer timescales (see Stuart and Jacobson, 2003, 2004, 2006). However, the cases of ammonia and formaldehyde emphasizes the importance of aqueous phase reaction kinetics when describing retention. Particularly, real cloud droplets are highly non-idealized mixtures of all kind of substances, which might interact with each other. Although the developed relationship of the retention coefficients on the effective Henry’s law constant is a large step towards a better representation of retention in cloud resolving models, the actual nature of the process is still not well understood. Beside the chemical point of view, retention contains many uncertainties arising from the solidification process. In particular, the interaction between the molecules and the developing ice is complex and depends on various parameters which by themselves are poorly understood, e.g. trapping of molecules in liquid volumes during crystallization, segregation of the molecules from ice, the formation of an ice shell along the surface of the droplets (which effectively hinders further degassing), and spreading of the droplets upon impact on the rime collectors. Finally, retention describes a combination of coupled processes, which need further laboratory and modeling efforts to better characterize them, also for wet-growth riming conditions such as the growth of hail.
Figure 1: Measured retention coefficient of SO$_2$ as function of ambient temperature. The solid lines represent the linear regression of the data and the 95% confidence bands. From von Blohn et al., 2013 with changes.

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REFERENCES


VISCOS SEC D ORG AER SLS ELEVAGE LG O LNG R RAN T AND LUNG -CANCER RISK

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Keywords: VISCOS ORGANIC SHIELD, ORGANIC AEROSOLS, HETEROGENEOUS CHEMISTRY, POLYCYCLIC AROMATIC HYDROCARBONS.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have toxic impacts on humans and ecosystems. One of the most carcinogenic PAHs, benzo (a) pyrene (BaP), is efficiently partitioned to and transported with atmospheric particles. Laboratory measurements show that adsorbed BaP degrades in a few hours by heterogeneous reaction with ozone, yet field observations indicate BaP persists much longer in the atmosphere, and some previous chemical-transport modelling studies have ignored heterogeneous oxidation of BaP to bring model predictions into better agreement with field observations. We attribute this unexplained discrepancy to the shielding of BaP from oxidation by coatings of viscous organic aerosol (OA). Accounting for this OA viscosity-dependent shielding, which varies with temperature and humidity, in a global climate/chemistry model brings model predictions into much better agreement with BaP measurements, and demonstrates stronger long-range transport, greater deposition fluxes, and substantially elevated lung-cancer risk from PAHs. Model results indicate that the OA coating is more effective in shielding BaP in the mid/high latitudes compared to the tropics because of differences in OA properties (semi-solid when cool/dry vs. liquid-like when warm/humid). Faster chemical degradation of BaP in the tropics leads to higher concentrations of BaP oxidation products over the tropics compared to higher latitudes. This study has profound implications demonstrating that OA strongly modulates the atmospheric persistence of PAHs and their cancer risks.

METHODS

We incorporate the two formulations (new, where OA coatings shield BaP from heterogeneous oxidation, and default, where OA does not shield BaP) within the global Community Atmosphere Model version 5.2 (CAM5). Simulations are performed for 2007 to 2010. A major fraction (generally ≥90%) of freshly emitted gaseous BaP is absorbed within co-emitted primary organic aerosol (POA) or subsequently formed secondary organic aerosol (SOA), or adsorbed onto co-emitted soot/black carbon (BC). At warm/humid conditions, BaP heterogeneous oxidation is assumed to be relative humidity (RH)-dependent based on laboratory measurements of BaP coated by SOA [Zhou et al., 2013]. At cool and/or dry conditions however, we assume that highly viscous OA effectively shields BaP from heterogeneous oxidation, similar to that observed for eicosane (a highly viscous solid organic) coatings [Zhou et al., 2012]. We use a global BaP emissions inventory from 2008 [Shen et al., 2013], and assign temporal and vertical profiles to BaP emissions in relevant source categories. Both secondary organic aerosol (SOA) and directly emitted primary organic aerosol contribute to the OA coating thickness, but SOA dominates the global budget of OA [Shrivastava et al., 2015]. While SOA is treated as liquid-like and semi-volatile in the default formulation, the new formulation treats SOA as a semi-solid and effectively non-volatile,
which has been shown to agree with a suite of global OA measurements [Shrivastava et al., 2015]. The simulated coating thickness of OA around the BC core is calculated in every model grid and time step and often exceeds the threshold of 20 nm for being classified as a thick coating. Model simulated coating thickness is within the range of reported measurements of OA coating thicknesses [Forrister et al., 2015]. We examined one PAH in particular as a representative of all PAH mixtures. Called BaP, this is one of the most carcinogenic PAHs.

RESULTS

We compared the simulation results to BaP field measurements from 69 rural sites and 294 urban sites worldwide. Each site included hundreds of measurements. Fig. 1 shows that BaP predictions from the new shielded modeling formulation were far more accurate than the default unshielded modeling formulation.

Fig. 1. Evaluation of 2008-2010 near-surface BaP concentration predicted by the default unshielded (red) and new shielded (blue) modelling formulations against field measurements of BaP. Model results for each site are averages over observation days. Top row shows scatter plots of simulated and observed concentrations at (a) 69 background/remote sites and (b) 294 non-background sites around the world [Borůvková J. et al., 2015; EMEP; IADN; Shen et al., 2014]. Modified normalized mean biases (MNMB) are calculated as in Wagner et al. [2015]. Areas of circles are proportional to the number of days sampled at each site.

To demonstrate the consequences of atmospheric long-range transport of BaP, we conduct several additional simulations in which BaP emissions from different source regions are turned on in the model, one at a time. Fig. 2 compares the long-range transport of BaP emitted from three major regions, East Asia, Western Europe and Africa, which together comprise 63% of global BaP emissions. Fig. 2 shows that the shielded PAHs (top rows) traveled much farther from their places of origin across oceans and continents, whereas in the previous unshielded model, they barely moved from their country of origin. The heterogeneous oxidation lifetime of PAHs was substantially increased from ~2 hours in the default unshielded model to ~5 days when they were shielded by viscous organic aerosols.
We then investigated the impact of PAHs on human health, by combining a global climate model, running either the shielded PAH scenario or the previous unshielded one, with a lifetime lung-cancer risk assessment model. Globally, the previous model predicted half a cancer death out of every 100,000 people, which is halfway to the limit set forth by the World Health Organization for PAH exposure. But taking into account that the shielded PAHs actually travel great distances, the new model found the risk was four times that, or two cancer deaths per 100,000 people, exceeding WHO standards. With a world population of about 7 billion people, that equates to a rise from about 35,000 lung cancer deaths to about 140,000.

Finally, we examined how the PAHs behaved within the coating of the aerosols at different locations around the globe. We found that the extent of shielding was much lower over the tropics compared to the mid and high latitudes. As the aerosols traversed the warm and humid tropics, ozone could get access to the PAHs and oxidize them. This was because the coating was more liquid than solid, thanks to warmer and more humid tropical weather, which allowed the PAHs to move freely in the particles. Future studies are needed to better understand how the shielding of PAHs varies with the complexity of aerosol composition, atmospheric chemical aging of aerosols, temperature and relative humidity.

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REFERENCES


Shen, H. Z., et al. (2014), Global lung cancer risk from PAH exposure highly depends on emission sources and individual susceptibility, Scientific Reports, 4, doi:10.1038/srep06561.


SESSION 16: AEROSOLS IN URBAN ENVIRONMENT

Imre Salma: Special features and relevance of new aerosol particle formation and growth process in cities

Wei Nie: New particle formation in polluted Yangtze River Delta

Xueshun Chen: Simulation on particle formation in Beijing

Chunguan Cui: Visibility, PM2.5 and relative humidity in Wuhan

Mao Xiao: Investigation of the role of aromatic hydrocarbons in new particle formation under urban atmospheric condition in the cloud chamber

Carmen Dameto de Espana: Long-term study of urban new particle formation events and their impact on cloud condensation nuclei
SPECIAL FEATURES AND RELEVANCE OF NEW AEROSOL PARTICLE FORMATION AND GROWTH PROCESS IN CITIES

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Keywords: nucleation strength factor, shrinkage of nucleated particles, secondary aerosol.

INTRODUCTION

New aerosol particle formation (NPF) and consecutive particle growth processes in the atmosphere were first identified in clean environments. Their frequency of occurrence and their contribution to particle number concentrations were later found to be substantial in the global troposphere. Particles originating from this process can affect the Earth’s radiation balance mainly by acting as cloud condensation nuclei, and their importance regarding the climate change is increasingly recognised. Recently, NPF has been proved to be common in polluted environments, also including large cities. As a consequence, nucleated particles can affect the public’s exposure to aerosol particle numbers in addition to their role in the urban climate system. Therefore, it is required to determine the characteristics of the NPF and particle growth specifically in cities, and to quantify their contribution to total particle number concentrations, for instance, with respect to emission sources.

METHODS

Particle number size distributions were measured by a flow-switching differential mobility particle sizer (DMPS) in the diameter range of 6–1000 nm with a time resolution of about 10 min in the city centre and near-city background of Budapest for 5 years in total, together with supporting gas pollutants and basic meteorological data. Most measurements were realized at Budapest platform for Aerosol Research and Training (BpART, Salma et al., 2016a). The overall treatment of the measured DMPS data was performed according to the procedure protocol recommended by Kulmala et al. (2012). Mathematically inverted size distributions were utilised for calculating particle number concentrations in the diameter ranges from 6 to 25 nm ($N_{6-25}$), from 6 to 100 nm ($N_{6-100}$), from 100 to 1000 nm ($N_{100-1000}$) and from 6 to 1000 nm ($N$). The individual size distributions were fitted by lognormal functions using the DoFit algorithm. The growth rate (GR) of particles in the size interval of 6–25 nm, and their shrinkage rate (SR) were determined by a log-normal distribution function method. The formation rate ($J_6$) of particles with a diameter of 6 nm, and condensation sink (CS) were computed according to Kulmala et al. (2012) and Dal Maso et al. (2002), respectively. The earliest estimated time of the beginning of nucleation ($t_1$), and the ending time of the particle growth process ($t_e$) were derived by a comparative method (Németh and Salma, 2014). The gas-phase H$_2$SO$_4$ proxy values were derived as [SO$_2$]×GRad/CS for intensities >10 W m$^{-2}$, where GRad is global solar radiation (Petäjä et al., 2009).

RESULTS AND CONCLUSIONS

Different types of size distribution surface plots for particle growth processes were observed during the 5 years of operation, including banana-shaped plots 1) with narrow onset, 2) appearing in a time window, 3) limited in time, 4) with multiple consecutive onsets or 5) with a broad continuous onset, and 6) arch-shaped plots. The latter type consists of an obvious and uninterrupted particle growth of nucleated
particles which was followed by a continuous decrease in nucleation-mode median diameter. It was identified in 4.5% of quantifiable nucleation events (on 8 days). The shrinkage phase took 1:34 h in general, and the SR varied from −4.8 to −2.3 nm h⁻¹ with a mean and standard deviation of (−3.8±1.0) nm h⁻¹. In some cases, the newly formed particles shrank back to the smallest measurable diameter limit of 6 nm. Concentrations $N_{6-25}$, $N_{6-100}$ and $N_{100-1000}$ increased substantially (by approximately 45–70%) during the particle growth phase - as expected, and they decreased by about 30–50% during the particle shrinkage phase. Variation in $N_{100-1000}$ over these time intervals were negligible. Changes of $O_3$, GRad, $H_2SO_4$ proxy, relative humidity, air temperature ($T$) and partially wind speed are biased by their ordinary diurnal cycling, and the atmospheric concentrations are also influenced by planetary boundary layer dynamics and mixing intensity. The largest relative changes expressed by the mean growth/shrinkage ratios were associated with GRad, $T$ and $H_2SO_4$ proxy. This indicates that there can be further relationships -- in addition to the diurnal bias -- between these variables on one side and the physicochemical processes undergoing within the particles during the shrinkage phase on the other side. The dependency can include decreased photochemical activity, or decreased concentration of gas-phase $H_2SO_4$ leading eventually to exhausted atmospheric supersaturation. Considering that the mean contribution of $H_2SO_4$ condensation to the particle GR was estimated to be only 12.3% in Budapest (Salma et al., 2016b), the explanation has to be extended by concentration decrease of other condensable vapours, mainly organic compounds. It is worth noting that for several arch-shaped plots, the mean $T$ was below 10 °C, and in one case, the shrinkage occurred at $T$ as low as −2.2 °C. These indirectly support the importance of highly oxygenated molecules (HOMs, Bianchi et al., 2016) in the particle growth process in real ambient air and, specifically, in cities. However, the shrinkage could not be fully explained by local atmospheric parameters. This implies that both major
ideas on the reasons for particle shrinkage (i.e. evaporation or variations in $J$ and GR during the atmospheric transport) could be effective.

The mean $N_{6-100}/N_{100-1000}$ concentration ratio averaged for nucleation days expresses the relative contribution of all emission sources and formation processes of ultrafine (UF) particles relative to the regional aerosol (represented by $N_{100-1000}$). At the same time, a similar concentration ratio derived for non-nucleation days expresses the relative contribution of all production processes of UF particles except for the NPF relative to the regional aerosol. Their ratio, which is called nucleation strength factor (NSF, Salma et al., 2014):

$$\text{NSF} = \left( \frac{N_{6-100}}{N_{100-1000}} \right)_{\text{nucleation days}} \left( \frac{N_{6-100}}{N_{100-1000}} \right)_{\text{non-nucleation days}}$$  \hspace{1cm} (1)

indicates the specific contribution of NPF relative to the regional background with respect to all sources. It was implicitly assumed in this reasoning that the major generation processes of particle number concentrations except for nucleation are uniformly present on both nucleation and non-nucleation days. If 1) NSF=1 then the relative contribution of nucleation to the UF particles with respect to other sources is negligible, 2) $1 < \text{NSF} < 2$ then its relative contribution is significant or considerable, and 3) NSF>2 then the relative contribution of nucleation itself to the UF particles is dominant (larger than of any other production processes together). Diurnal variations of NSF in the city centre separately for spring, summer and autumn seasons are shown in Figure 2a, while the diurnal variation of concentrations $N_{6-100}$ and $N_{100-1000}$ separately for nucleation days and non-nucleation days in spring are displayed in Figure 2b.

![Figure 2](image-url)

**Figure 2.** Mean diurnal variation of nucleation strength factor separately for spring, summer and autumn seasons (a) and of particle number concentrations $N_{6-100}$ and $N_{100-1000}$ separately for nucleation and non-nucleation days in spring (b) for the city centre for 1-year interval in 2014–2015. The horizontal line indicates the value above which the NPF becomes the major source for UF particles.

It is seen that the NSF curves exhibit a single peak around 13:00 (local daylight saving time). The baselines of the peaks (from 0:00 to 8:00) for spring and summer fluctuate around 1.00 in accordance with the assumption above. Its validity for spring can also be observed in detail in Figure 2b. The baselines for autumn and in particular for winter (not shown) were at a higher level. This can be explained by the fact that either the pre-existing UF particles on nucleation days are in larger concentration than for non-nucleation days, which is unlikely, or that the particle number concentration of the regional aerosol is smaller for nucleation days than for non-nucleation days. The latter option implies that nucleation events preferably take place on days characterised with smaller particle number concentrations, which is in line
with general ideas on NPF’s driving forces. Daily mean NSFs and standard deviations in the city centre for 1-year long intervals in 2008–2009 and 2013–2014 were 1.49±0.35 and 1.44±0.40, respectively, while in the near-city background for 2012–2013, they were 2.3±1.2. This means that the NPF and particle growth process is a non-negligible source of UF particles relative to their all sources and formation processes even in the city centre, and it becomes the dominant source in the background. During the midday hours, the UF contribution of NPF was similar to other production types — including traffic emissions. This emphasizes the need to study the health consequences of particles originated from NPF and growth events in cities in addition to their (urban) climate relevance.

ACKNOWLEDGEMENT

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REFERENCES


NEW PARTICLE FORMATION IN POLLUTED YANGTZE RIVER DELTA


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Keywords: NEW PARTICLE FORMATION, HETEROGENEOUS, DUST, YANGTZE RIVER DELTA

INTRODUCTION

Atmospheric new particle formation (NPF) and growth have been demonstrated to be an important source of atmospheric aerosols and play important roles in climate (e.g. Dunne et al., 2016). Previous understanding believes NPF prefer occurring in clean environment (Kulmala et al., 2004). High concentration of pre-exist particles would uptake low volatile vapers and newly formed clusters, and in turn suppress the particle nucleation and subsequent growth.

Recently, NPF has been more and more observed in polluted regions (Nie et al., 2014; Qi et al., 2015; Xiao et al., 2015), and even contributed largely to aerosol pollution (Guo et al., 2014). But the mechanism of these NPF under polluted condition is still far from understanding (Kulmala et al., 2016). In this work, we focus on the long term NPF observation at a station in polluted Yangtz River Delta, and the possible “new” chemical processes related to atmospheric oxidation capacity and secondary aerosol formation.

METHODS

A long term and comprehensive measurement was conducted from 2011 at the SORPES “flagship” central site in Xianlin of Nanjing (Ding et al., 2013&2016). It is a regional background site, located on the top of a hill (118°57’10” E, 32°07’14”, 40 m a.s.l.) in the Xianlin campus of Nanjing University and about 20 km east of the suburban Nanjing city. NPF related parameters, including particle size distribution (from 1 nm to 10000 nm), chemical compositions (water soluble ions, OC and EC), trace gases (O₃, NOₓ, SO₂, HONO et al.) and meteorological quantities were measured. Besides the long term
measurement at SORPES site, some intensive campaigns were also conducted focusing on some heterogeneous processes, e.g. a campaign during the spring in 2009 at the top of Mt. Heng with the target on Asian dust.

CONCLUSIONS

A high frequency of NPF events, up to 44% of the sampling days, have been observed at SORPES station. The occurrence of NPF was limited mostly by the meteorologic condition but not precursors. Compared to clean area, sulfuric acid was a more important contributor to particle nucleation and initial growth in Yangtze River Delta.

As showed in Fig. 1, many of the NPF events occurred on the days with heavy aerosol pollution (PM$_{10}$ more than 200 μg cm$^{-3}$), especially when dust plums influenced the station. Further analysis suggested dust particles can induce heterogeneous photochemical processes, which in turn promote the formation of HONO and new particles (Nie et al., 2012, 2014, 2015). These processes can be largely enhanced once the dust particles are “polluted” by anthropogenic pollutions.

Figure 1 Time series of PM, trace gases, calcium, sulfate, aerosol size distributions, and meteorological parameters measured during May 2012 at SORPES station.
A certain class of NPF events, defined as early-morning NPF, was observed at SORPES station in YRD of east China. This early-morning NPF occurred only a few minutes after sunrise. Highly Oxidized Multifunctional organic molecules (HOMs) and radicals produced from monoterpene oxidation were considered to play an important role (Mikael et al., 2014; Yan et al., 2016).

ACKNOWLEDGEMENTS

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REFERENCES


Nie, W. et al. Asian dust storm observed at a rural mountain site in southern China: chemical evolution and heterogeneous photochemistry. Atmos. Chem. Phys. 12, 11985-11995, doi:10.5194/acp-12-11985-2012 (2012).


Simulation on particle formation in Beijing

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Keywords: NAQPMS+APM, nucleation, primary emission, particle number size distribution

INTRODUCTION

The large scale haze that has occurred in China in recent years has drawn much public concern. In these pollution events, the concentration of fine particles has reached unprecedentedly high levels across many cities (Huang et al., 2014; Wang et al., 2013). Beijing, the capital of China, is a typical city suffering from such fine particle pollution (Quan et al., 2014). The Beijing Environmental Protection Agency reported that particulate matter was the dominant pollutant in the urban atmosphere of Beijing. Understanding the physical and chemical mechanism of fine particle formation presents an import challenge. A basic step toward solving the pollution problem is to acquire comprehensive information on fine particle parameters and to understand the particle formation mechanism. The impact of local emissions and regional transport on particle mass concentration in Beijing has been fully analyzed in previous studies (Ma et al., 2012; Zhao et al., 2009; Shen et al., 2014). For particle number concentration, Wehner et al. (2004) investigated size distributions and their variability in Beijing. Wu et al. (2008) analyzed two-years of measurements of PNSD (3 nm-10 μm) in Beijing and found that the diurnal variation of nucleation mode particles was mainly influenced by nucleation events in winter while the diurnal variation of Aitken mode particles closely correlated with traffic densities, indicating the varied contribution of different sources to particle number concentration in different size ranges. Zhang et al. (2011) compared particle growth rates influenced by pollution controls, suggesting that decreased growth rates during the Olympic Games in Beijing were due to the combined effects of weather and lower concentrations of precursor gases. Using a parameterized nucleation scheme in WRF/Chem, Matsui et al. (2011) showed that new particle formation contributed 20-30% of the particle number concentrations (>10 nm in diameter) in and around Beijing on average in a summer period. Peng et al. (2014) estimated the contribution of new particle formation to CCN at 0.2% super-saturation to be 11% and 6% at urban and regional sites by investigating PNSD at 13 different sites over China. Other studies have investigated particle size distributions, formation rates and growth rates (e.g., Yue et al., 2009; Shen et al., 2011). However, comprehensive studies of the relative contribution of nucleation and primary emission and their roles in particle formation in polluted atmosphere in haze season are still scarce (Ma et al., 2012). In contrast to these previous studies, the NAQPMS+APM model can explicitly resolve newly formed secondary particles via nucleation and primary particles from direct emission based on full microphysics (Yu and Luo, 2009; Chen et al., 2014). Therefore, the model can be used to quantify the contributions of nucleation and direct emission to particle number concentration in different size ranges and thus explore their different roles in contributing to particulate pollution. The main goal of this paper is to identify the key factors governing PNSD formation in the polluted atmosphere in Beijing and surrounding areas.

METHODS
The NAQPMS+APM model is a three-dimensional air quality modeling system with a full treatment of chemical processes for gases and detailed microphysics for aerosol particles to describe regional and urban scale atmospheric pollution (Chen et al., 2014). NAQPMS+APM is developed from the Nested Air Quality Prediction Model System (NAQPMS) and the Advanced Particle Microphysics (APM) model. NAQPMS is a 3D Eulerian chemical transport model with terrain-following coordinates, developed by the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP/CAS). It includes modules accounting for horizontal and vertical advection, diffusion, dry and wet deposition, gaseous chemistry, aqueous chemistry and heterogeneous chemistry (Wang et al., 2000; Li et al., 2011). APM is an aerosol model with detailed microphysics to describe nucleation, condensation and coagulation (Yu et al., 2009). In the model, ion-mediated nucleation (IMN) is used because it is physically-based and constrained by laboratory data (Yu, 2006), and it predicts global nucleation distributions with a reasonable consistency (Yu et al., 2008). In NAQPMS+APM, the condensation of H2SO4 on particles is explicitly resolved while the uptake of nitrate, ammonium and secondary organic species is considered through equilibrium partitioning. For simplicity, coating species (i.e. sulfate, nitrate, ammonium and semi-volatile organics) on seeding particles are tracked using a bulk method. Mass concentrations of nitrate and ammonium are calculated using an aerosol thermodynamic equilibrium partition model (Nenes et al., 1998). A bulk yield scheme is used to represent the formation of secondary organic aerosols (SOA) (Li et al., 2011). The amounts of nitrate, ammonium, and SOA partitioned to secondary particles in each bin and the coating mass associated with primary particles are assumed to be proportional to the corresponding sulfate mass.

In this study we use three nested modeling domains, with the first domain covering East Asia at 81 km resolution, the second domain covering central and eastern China at 27 km resolution, and the third domain covering Beijing and surrounding areas at 9 km resolution. There are 20 layers in the vertical, with high resolution near the surface and model top at 20 km. The meteorological input fields are produced by the Weather Research and Forecasting model (WRF). WRF is driven by static geographical data and Final Analysis (FNl) datasets from the National Centers for Environmental Prediction (NCEP). Emission data are from the regional emission inventory in Asia version 2 (REAS2) (Kurokawa et al., 2013). The simulation period is from January 1 to February 13, 2006. The first 15 days of simulation are excluded from analysis in order to limit the effect of the initial condition. Therefore, simulation results from January 15 to February 13 are presented in this study. Since this study mainly focuses on Beijing and surrounding areas, only results of the third domain are presented. Following Wu et al.(2007), the size ranges for the nucleation mode, Aitken and accumulation modes in this study were 3-25nm, 25-100nm, 100-1000nm, respectively. We use the term 'total particles' to refer to particles with diameters from 3nm to 1000nm. The term 'all particles' refers to all types of particles, including both primary and secondary particles.

The experiments for analysis in this study include a control run, BASE, and four sensitivity runs, listed in Table 1. From BASE experiment, the characteristics of the PNSD and number concentration in different modes (seen in Fig.1) were analyzed; In SEN1-1, nucleation was shut off over the whole modeling domain in order to analyze the effects of nucleation on PNSD; In SEN1-2, nucleation was shut off in Beijing only in order to investigate the spatial influence of nucleation and secondary particles formation in Beijing on PNSD. In SEN2-1, primary particle emissions were shut off over the whole modeling domain in order to analyze the effects of primary emitted particles on PNSD; In SEN2-2 primary particle emissions were reduced by 50% over the whole modeling domain to analyze the effects of emission reduction on air quality in terms of particle number concentration. All simulations were performed with the same model configuration except for the variations described above.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE</td>
<td>IMN with primary emission</td>
</tr>
<tr>
<td>SEN1-1</td>
<td>Turn off nucleation</td>
</tr>
<tr>
<td>SEN1-2</td>
<td>Turn off nucleation in Beijing</td>
</tr>
<tr>
<td>SEN2-1</td>
<td>Turn off primary emissions</td>
</tr>
<tr>
<td>SEN2-2</td>
<td>Reduce primary emission by 50%</td>
</tr>
</tbody>
</table>
CONCLUSIONS

In this study, the characteristics of aerosol particle number concentration in Beijing were investigated using NAQPMS+APM. The number concentration of total particles was observed to be 26581 cm$^{-3}$ and simulated as 39784 cm$^{-3}$ in simulation (see Table 2), indicating severe fine particle pollution compared with other large cities worldwide (Wu et al., 2008). From the observation data and baseline simulation, we find that nucleation mode particle number concentrations are mainly controlled by nucleation while Aitken mode particle number concentrations are determined by both nucleation and primary emission. In the accumulation mode, primary particles dominate the particle number concentration. Due to the long lifetime of accumulation mode particles, their temporal evolution is affected by meteorological conditions. The spatial pattern of nucleation mode particles follows the distribution of secondary particles while the spatial pattern of the Aitken and accumulation modes follow the distribution of primary particles. Over Beijing and surrounding areas, secondary particles contribute at least 80% of the number concentration in the nucleation mode and 20-80% in the Aitken mode while their contribution to accumulation mode particles is only 10-20%.

From sensitivity experiments, we find that nucleation has more obvious effects on ultrafine particles while primary particle emissions are efficiently in producing large particles in the accumulation mode. Nucleation or primary emissions alone could not explain the formation of the PNSD in Beijing. In the surface atmosphere, the effect of nucleation is mainly limited to the local scale. With particle size increases, the distance influenced by nucleation is increased. Reduction of primary particle emissions may not always lead to a decrease in the particle number concentration due to the increase of the number concentration of secondary particles through nonlinearity in the microphysical processes. Yu (2010) pointed out that the emission controlling strategy aiming to reduce particles mass may lead to the increase in new particle formation and thus particle number concentration. Spracklen et al. (2006) showed that European particle number concentration can be increased by reducing primary particle emission. Measures to reduce fine particle pollution focusing on particle number concentration need to be different from those addressing particle mass concentration. It is necessary to reduce the precursors favorable for new particle formation and particle growth in order to reduce particle number concentration.
**FAAR abstract instructions and template**

*Please read carefully - the text contains instructions for abstract preparation*

Table 2 Mean number concentration and correlation coefficient for different modes in Beijing

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Nucleation mode</th>
<th>Aitken mode</th>
<th>Accumulation mode</th>
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<tbody>
<tr>
<td></td>
<td>Conc(cm(^{-3}))</td>
<td>R</td>
<td>Conc(cm(^{-3}))</td>
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<tr>
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<td>13038</td>
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<tr>
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<td>13476 0.71</td>
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<td>12683 0.71</td>
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<tr>
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<td>19567 0.30</td>
<td>13233 0.71</td>
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<tr>
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<td>8134 0.08</td>
<td>3635 0.59</td>
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<tr>
<td>SEN2-2</td>
<td>4693 0.71</td>
<td>15451 0.33</td>
<td>9653 0.70</td>
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</table>

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We thank Prof. Min Hu's group at the College of Environmental Sciences and Engineering, Peking University for support with the observation data. We are particularly grateful to Prof. Wild Oliver in Lancaster University for his help in improving the language of this manuscript. This work was supported by the Chinese Key Projects in the National Science & Technology Pillar Program (2014BAC06B03), the Chinese Academy of Sciences Strategic Priority Research Program (XDB05030101,XDB05030200),and the Natural Science Foundation of China (41225019 and 41275138).

REFERENCES


Study on the nonlinear relationship among the visibility, PM2.5 concentration and relative humidity in Wuhan and the visibility prediction

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Keywords: PM2.5, Visibility, Relative humidity, Nonlinear relationship.

INTRODUCTION

Abstract: The air pollution and haze events occur frequently in Wuhan, a city with particularly high humidity in central China. And the quantitative relationships were still uncertain among the atmospheric visibility, the PM2.5 concentration, and the relative humidity (RH). Based on the hourly observed datasets of visibility, RH, and particulate mass concentration in Wuhan from September 2014 to March 2015, the relationships mentioned above as well as the nonlinear prediction of visibility are studied. It is detected that the frequent occurrence of haze in Wuhan and its aggravation seriously reduce the visibility. The formation and accumulation of fine particulate are also important inducing factors of that. The variation of atmospheric visibility is under the joint influence of RH and particulate mass concentration. High values of RH and fine particulate mass concentration may bring about the significantly decreasing of the variability. Under the wet conditions (RH ≥ 40 %), the increasing RH leads to the growth of moisture absorption of the fine particulate, which can result in the increasing scattering rates of them, then the visibility deterioration occurs. When RH is higher than 90 %, the linear decreasing of visibility along with the increasing RH can be presented as that an RH increasing by 1% reduces the visibility value by 0.568 km averagely. Under the dry conditions (RH < 40 %), the increasing PM2.5 concentration is the critical factor of the rapidly decreasing visibility. Under urban pollutions of the fine particulate in the atmosphere, the visibility has a nonlinear relationship with RH, which may be associated with the influence of PM2.5 in the visibility as well as the scattering rate variation of hygroscopic particles. Results also indicate that the nonlinear relationship between the PM2.5 concentration and the visibility is shown as a power function. The correlation is most significant when the RH is less than 90 % and no less than 80 %. The sensitive threshold of PM2.5 concentration for the atmospheric visibility is reduced along with increasing RH. Corresponding to the visibility of 10 km, the threshold is 70 μg/m³ under the dry conditions, while the value is among 18-55 μg/m³ under the wet conditions. The decreasing PM2.5 concentration can contribute to the higher visibility even when it is less than 40 μg/m³. Additionally, the visibility prediction model based on the neural network method performs well in the preliminary experiments. The correlation coefficient is up to 0.86, and the Root Mean Square Error (RMSE) is 1.9 km. The TS score is 0.92 when the visibility is no larger than 10 km. Evidences indicate that the model has a positive skill for the haze prediction. It provides a powerful reference for the cohesion of regional numerical prediction models of
environment and meteorology, and the establishment of refined statistical-dynamical prediction model of the atmospheric visibility.

Figure 1. The correlation between the visibility and PM2.5 concentration in different relative humidity ranges in Wuhan.

Figure 2. The correlation between the relative humidity and visibility in Wuhan.
Figure 3. The distribution of visibility and the scatters for relative humidity versus PM2.5 concentration in Wuhan.

Figure 4. Comparison between observed and simulated hourly visibility using the neural network model during training (a) and forecasting (b) period in Wuhan.
REFERENCES


INVESTIGATION OF THE ROLE OF AROMATIC HYDROCARBONS IN NEW PARTICLE FORMATION UNDER URBAN ATMOSPHERIC CONDITION IN THE CLOUD CHAMBER

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Keywords: NEW PARTICLE FORMATION, CHAMBER, AROMATIC, NUCLEATION.

INTRODUCTION

Atmospheric aerosols play an important role in climate forcing by affecting radiative balance and cloud formation. They are also of concern because of their impact on visibility and human health. New particle formation (NPF), as one of the major sources of atmospheric aerosols, has a great effect on the particle number concentration and size distribution. Despite its significant contribution to the regional and global aerosol budget, the understanding of physical and chemical mechanisms behind the NPF process is still poor.

The CERN CLOUD chamber facility was used to study mechanisms of NPF because it has a low level of contamination and a good control of experimental parameters. Binary nucleation between sulfuric acid and water (Kirkby et al., 2011), ternary nucleation of sulfuric acid, water with ammonia (Kirkby et al., 2011) or dimethylamine (Almeida et al., 2013), pure biogenic nucleation (Kirkby et al. 2016; Tröstl et al. 2016; Dada et al., this abstract collection) as well as nucleation of sulfuric acid, ammonia together with oxidation products from biogenic precursors (Riccobono et al., 2014; Lehtipalo et al., this abstract collection) were investigated systematically. The results from those studies led to great advancement in resolving chemical and physical mechanisms of NPF. However studies based on the conditions of urban atmospheres, where huge populations are exposed to high aerosol concentrations, are still missing and are urgently needed.

In contrast to remote sites such as a boreal forest, urban atmospheres are highly polluted with high concentrations of sulfuric acid, ammonia, NOx and volatile organic gases from anthropogenic activity as well as high particle concentrations, which provide a high condensation sink for condensable gases. Photochemical air pollution in the urban atmosphere is often dominated by anthropogenic volatile organic compounds (AVOC), containing a high fraction of aromatic hydrocarbons (ArHC) originating from industrial activities, traffic or residential wood combustion. Highly oxygenated molecules (HOMs) formation from OH-triggered autooxidation of ArHC has been observed in a recent study (Molteni et al., 2016). Fig. 1 shows the formation of HOMs from the reaction of OH with ArHC. HOMs from the oxidation of biogenic precursors were found to initiate nucleation and early particle growth (Kirkby et al., 2016; Tröstl et al., 2016). Therefore, we suspect that HOMs from ArHC could contribute to NPF events detected in urban areas. Chamber experiments using 1,3,5-trimethylbenzene (1,3,5-TMB) and SO2 conducted at the PSI environmental chamber already demonstrated the potential of NPF of such a system (Metzger et al. 2010) but no HOMs were measured due to limitation in instrumentation at that time. There were also several parameters such as the effect of carbon number of ArHC precursor, NO, and ammonia missing in their study.
Figure 1. Mass defect plot of triggered ArHC HOMs, modified from Molteni et al. (2016).

In this study we investigated the potential of ArHC in NPF under controlled experimental conditions relevant to the urban atmosphere. Experiments were conducted in the CLOUD chamber. Multiple AVOC vapors were tested as precursors and systematically mixed with other relevant trace gases like SO₂, ammonia and NOₓ to obtain an understanding and parameterization of the AVOC NPF system.

METHODS

The experiments were conducted at the CERN CLOUD chamber facility during the CLOUD11 campaign in fall 2016. To understand the effects of carbon number of precursors, three ArHC were selected in this study: toluene, 1,2,4-trimethylbenzene (1,2,4-TMB) and naphthalene (NPT). To better represent the urban atmosphere, experiments were also conducted with mixtures of these ArHC. All the experiments were conducted in the presence of sulfuric acid concentrations between 1E07 cm⁻³ to 2E08 cm⁻³ with or without the addition of ammonia (> 500 ppt) and NOₓ (from 0 to 25 ppb). In a systematic way different combinations of ArHC precursors and the other trace gases were tested in the experiments as summarized in Table 1: single VOC together with sulfuric acid, single VOC together with sulfuric acid and ammonia, single VOC together with sulfuric acid, ammonia and NOₓ, mixture of the three VOCs together with sulfuric acid, ammonia and NOₓ. OH (from 1E06 cm⁻³ to 1E07 cm⁻³) was generated by O₃ photolysis.
Most experiments were conducted with ionization from natural galactic cosmic rays (GCR) as in the real atmosphere. A few experiments were repeated either in neutral conditions by artificially removing ions using an electric field or under conditions with additional ionization from the CERN pion-beam. All experiments were conducted at 25 °C; mostly at 60% RH with a few experiments repeated at 30% RH and 80% RH.

Experiments were conducted under well controlled conditions. A PTR-TOF was used to measure the ArHC vapors concentrations. Chemical ionization mass spectrometers measured sulfuric acid and HOMs concentrations in the gas phase. Ion clusters were measured with two atmospheric pressure interface time-of-flight mass spectrometers (AP-TOF) running in positive or negative modes. SO₂, O₃ and NOₓ were measured with dedicated gas monitors. Particle number concentration and size distribution were obtained from several particle size magnifiers (PSMs) and CPCs, a DMA-train, a NAIS, an R-DMA and two SMPS-systems, from which the particle formation rate and growth rates were calculated. Particle phase chemical information was also obtained from state of the art mass spectrometers.

<table>
<thead>
<tr>
<th>Presence of System</th>
<th>NPT</th>
<th>1,2,4-TMB</th>
<th>Toluene</th>
<th>Sulfuric acid</th>
<th>ammonia</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>System I</td>
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<td></td>
<td>x</td>
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<tr>
<td>System II</td>
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<td>x</td>
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<td>x</td>
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<tr>
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<td>x</td>
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<td>System IV</td>
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</tr>
</tbody>
</table>

Table 1. A list of chemical systems studied.

CONCLUSIONS

All three ArHCs form HOMs. Their concentration and composition is influenced by the NOx concentration (see also Garmash et al., this abstract collection). New particle formation rates and early growth rates were derived for each of the precursors and their mixture with sulfuric acid. These NPF processes were modulated by ammonia and NOx. The effects of ion concentration and humidity will be reported.

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REFERENCES


LONG-TERM STUDY OF URBAN NEW PARTICLE FORMATION (NPF) EVENTS AND THEIR IMPACT ON CLOUD CONDENSATION NUCLEI (CCN)

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Keywords: New Particle Formation, Cloud Condensation Nuclei, Long-term study, Urban Aerosol.

INTRODUCTION

Observations and model studies (e.g. Kerminen et al., 2012) have demonstrated that New Particle Formation (NPF) events can be an important source of cloud condensation nuclei (CCN) in the atmosphere. However, the observations often only consider particle growth to a certain threshold in size distribution measurements. Just few studies (e.g. Asmi et al., 2011, Wiedensohler et al., 2009), have linked observed NPF and growth events directly to increases in measured CCN concentrations. Clearly, there is a lack of continuous long-term parallel measurements of CCN concentrations and of NPF events particularly in urban aerosols. Here, we present a 19-month CCN study embedded in a long term study of NPF events in the urban background.

METHODS

Atmospheric aerosol measurements are performed in the rooftop laboratory of the Faculty of Physics in the urban background of Vienna. Continuous size distribution measurements in the range of 10 – 600 nm have been conducted from September 2007 until December 2008 and from March 2012 until December 2016 with a Vienna type Differential Mobility Particle Sizer (DMPS) and an SMPS 3082 (TSI, Inc.) Simultaneous CCN concentration measurements were carried out from June 2014 to December 2015 with the Vienna Cloud Condensation Nuclei Counter (CCNC) (Dusek et al., 2006) operated at a nominal supersaturation of 0.5%. Total particle number concentrations were tracked to determine the activation ratio. Black carbon (BC) concentrations were measured with a Multi Angle Absorption Photometer (MAAP, Thermo Scientific) and used as tracer for traffic emissions. Hourly meteorological data were provided by the Central Institute for Meteorology and Geodynamics (ZAMG) situated 1 km north (Station: Hohe Warte) of the laboratory. Recorded size distributions were analysed in 24-hour sets spanning from midnight to midnight. The criteria by Dal Maso et al., 2005 were used to classify size distributions into event days, non-event days and undefined days.

RESULTS

Most of the NPF events happened during spring and summer. For example, in 2014 and 2015, events were observed on 69 (i.e. 13%) of the 539 measurement days, which is similar to the results presented in the study by Wonaschütz et al. (2015) and lower than in other central European long-term urban studies (Skrabalova et al., 2015). The results of the monthly size distribution classification for 2014 and 2015 are shown in Figure 1.
During the simultaneous CCN measurements in 2014 and 2015, 69 events were observed, and in 38 events, CCN concentration data were sampled to evaluate the impact of NPF on CCN concentrations. In the urban background, NPF events and the continuing growth of the newly-formed particles are sometimes superimposed by local pollution plumes. Traffic emissions could additionally increase the concentration of particles during a NPF event and CCN concentrations can vary due to weather conditions.

In order to study the impact of NPF on CCN concentrations, CCN concentrations before and after an event were compared when no changes in local emissions were observed and weather conditions before and after the event were similar. Figure 2 shows a contour plot of particle size distribution and a time series of the CCN concentration, observed on an event day where CCN concentrations before and after the event were compared. In 17 occasions, increases in CCN concentrations after event were observed.

Figure 1. Monthly size distribution classification for 2014 and 2015

Figure 2. CCN concentration during a NPF
CONCLUSIONS

From the 38 evaluated NPF events with CCN data, BC concentrations and weather conditions were unchanged before and after the events in 17 occasions. In these cases, CCN concentrations after and before the event could be compared. Changes in CCN concentrations could, however, have occurred also by changes in boundary layer height or air mass. To take into account these influences, selection criteria were developed (Dameto de Espana et al., 2017). Applying these criteria, NPF was found to be a source of CCN in 14 of the 17 events in the urban background of Vienna.

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REFERENCES


SESSION 17:
NUCLEATION: THEORY, EXPERIMENTS AND OBSERVATIONS

David Reguera: Nucleation under strong confinement

Tinja Olenius: Description of nucleation in aerosol dynamics models:
Evaluation of commonly used assumptions

Jorge Ferreiro: Direct observation of cluster size distributions during
nucleation and growth in laval expansions

Eimear Dunne: A new parameterization of inorganic nucleation

Clémence Rose: Atmospheric evidence for pure biogenic nucleation

Lubna Dada: Influence of atmospheric conditions on pure biogenic
nucleation in the CLOUD chamber
NUCLEATION UNDER STRONG CONFINEMENT

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Keywords: Classical Nucleation Theory, Superstabilization, Tolman length, Rigidity constants.

INTRODUCTION

Nucleation is the first and crucial step that controls first order phase transitions, such as cavitation, condensation or crystallization. It is central in many phenomena in atmospheric science, and several processes in nature and industry rely on quantitative predictions of nucleation rates. Despite of several extensions and theoretical advances, Classical Nucleation Theory (CNT) is still the most widely used theoretical tool to predict nucleation rates. However, although CNT provides a qualitatively correct picture of the process, its quantitative predictions are often orders of magnitude away from experiments.

Proper predictions of nucleation rates rely on a precise knowledge of the properties of the metastable phase and on an accurate evaluation of the surface tension of small droplets or bubbles. While equilibrium properties of fluids are experimentally available, it is a challenge to measure the properties of small, metastable phases. By their own labile nature, they tend to transform to a stable new phase via a nucleation process which is specially fast in the vicinities of the spinodal. However, confinement can help to defer phase transitions (Reiss et al., 1988) and to stabilize bubbles and droplets (Yang, 1985; Neimark and Vishnyakov, 2000).

In this presentation, we will discuss some of the particularities of nucleation under strong confinement. We will show that it is not only possible to delay these phase transitions, but to go one step further and completely impede nucleation in small confined systems. We shall discuss the conditions required for this superstabilization of fluids under which we can obtain infinitely long-lived metastable phases. At these conditions, the properties of the metastable fluid can be investigated in simulations and experimentally, facilitating the development of accurate equations of state for metastable regions, the evaluation of curvature corrections to the surface tension, and even a precise location of the spinodal.

RESULTS

We have performed a careful thermodynamic analysis of how phase transitions take place in closed systems, i.e. in the canonical ensemble, rather than at the usual open conditions, where pressure or chemical potential are controlled (Wilhelmsen et al., 2014a; Wilhelmsen and Reguera, 2015). We have used the modified bubble/droplet model (Reguera et al., 2003) to evaluate the nucleation barrier and the properties of the stable and critical cluster for condensation and cavitation in small spherical containers. Remarkably, when the system is strongly confined, there exists a minimum radius $R_{\text{min}}$ of the container below which no stable or critical cluster can form, signalling the onset of this superstabilization effect (Wilhelmsen et al., 2014a). As an example, Fig. 1 plots the
minimum radius of the container below which cavitation and condensation become impossible for water at 300 K.

A second important consequence of nucleation under strong confinement is the possibility of stabilizing very small bubbles and droplets. At those conditions, curvature corrections to the surface tension become relevant. These curvature corrections have been long suspected to be a crucial missing ingredient in CNT. But the proper evaluation even of the sign of the leading order correction, the Tolman length, is not well known, not even for a reference model as the Lennard-Jones fluid or for the most studied fluid: water.

Curvature contributions to the surface tension up to second order can be taken into account through the Helfrich expansion:

$$
\sigma(J, K) = \sigma_0 - \delta \sigma_0 J + \frac{k}{2} J^2 + \tilde{k} K + ...
$$

where, $\sigma_0$ is the surface tension of the flat surface, $J = \kappa_1 + \kappa_2$ is the total curvature, and $K = \kappa_1 \kappa_2$ is the Gaussian curvature, being $\kappa_1$ and $\kappa_2$ the principal curvatures. The magnitude of the curvature corrections in this expansion are defined by the Tolman length $\delta$, the bending rigidity $k$ and the rigidity constant $\tilde{k}$ associated with the Gaussian curvature.

We recently calculated these constants for the Lennard-Jones fluid and water (see Fig. 2), combining Square Gradient Theory (SGT) (Blokhuis and van Giessen, 2013) with a very accurate equation of state, and showed that we could then reproduce the Tolman length and surface tension obtained from MD-simulations (Wilhelmsen et al., 2015). The work also showed that the second order terms, the rigidity constants, were crucial to correctly predict the surface tension of small droplets and bubbles.

Furthermore, we showed that by properly including the curvature-dependence of the surface tension in CNT, it is possible to provide quantitatively accurate predictions of the experimental water nucleation rates with the correct temperature trend (see Fig. 2). Thus, at least for water, the proper incorporation of curvature corrections seems to correct some of the problems in CNT and brings hope that the same is possible for other substances.
Figure 2: The Tolman length (a) and the coefficients in the Helfrich expansion for water (b) from square gradient theory combined with the CPA equation of state (solid line) and from a linear extrapolation (red dashed line). The Tolman length calculated by Joswiak et al. (2013) (square) for TIP4P/2005 water is also included. (c) Experimental water nucleation rates from Wölkl and Strey (2001) (blue diamonds), Manka et al. (2010) (red circles), Brus et al. (2008, 2009) (pink and green triangles), Manka (2011) (yellow squares), and Wysloužil et al. (2007), for the temperatures $T = \{320, 310, 300, 270, 260, 250, 240, 230, 220\}$, compared to CNT (red dashed lines) and to CNT using curvature corrections (solid lines).

CONCLUSIONS

We have analyzed how nucleation takes place under strong confinement. We have shown that condensation and cavititation can be completely prevented in small closed containers. It is thus possible to keep fluids indefinitely at strongly metastable conditions that would lead to immediate nucleation in large or open volumes. At these conditions, that are experimentally feasible, it would be possible to control and prevent the explosive boiling of liquids, the cavititation of overstretched fluids, and to measure accurate equations of state for fluids in deeply metastable regions. This would thus have striking consequences in a wide variety of scientific and industrial phenomena.

In addition, we have calculated the Tolman length and rigidity constants of Lennard-Jones fluids and water using square gradient theory combined with an accurate equation of state. Using these constants, it is then possible to incorporate the curvature-dependence of the surface tension into the CNT-framework. The resulting predictions seem to correct the wrong temperature dependence of the nucleation rates given by the classical theory and also improve the agreement with experiments. Although, under some conditions, other corrections may also be relevant, this procedure offers a
promising way to alleviate the problems of CNT and obtain quantitatively accurate predictions.

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REFERENCES


Manka, A. Phase transitions of water from vapor to supercooled droplets to ice, Ph.D. thesis (University of Cologne, 2011).


DESCRIPTION OF NUCLEATION IN AEROSOL DYNAMICS MODELS: EVALUATION OF COMMONLY USED ASSUMPTIONS

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Keywords: Nucleation rate, applications, aerosol dynamics modeling, climate modeling.

INTRODUCTION

Nucleation is recognized as a significant source of atmospheric aerosol particles and cloud condensation nuclei. Understanding the initial steps of the new-particle formation process, in which nanometer-sized particles are formed from vapor molecules, is thus a pre-requisite for understanding the climatic effects of the particles. Recent progress in both theoretical and experimental approaches has led to more accurate estimates on the formation rate of particles of ~1–2 nm in diameter from atmospheric condensable vapors, and climate and air quality models have started to apply the state-of-the-art formation rate schemes for an improved description of nucleation (e.g. Baranizadeh et al., 2016; Dunne et al., 2016).

However, applying the results of nucleation theories or simulations in aerosol dynamics models, that simulate the time evolution of the particle population after the initial formation, involves certain assumptions and approximations. In this work (Olenius and Riipinen, 2017), we present a brief review of the assumptions, and systematically evaluate them for different atmospheric environments using a molecular-resolution particle population model. The results address the following question: if the formation rate obtained with an accurate nucleation model is implemented in an accurate aerosol dynamics model, how large are the uncertainties that arise solely from using the common assumptions made in incorporating the nucleation rate?

ASSUMPTIONS RELATED TO DESCRIBING NUCLEATION IN AEROSOL DYNAMICS MODELS

In new-particle formation modeling, the formation rate of the initial ~1–2 nm particles is predicted by a molecular model or parameterization, and the newly formed particles are then introduced in an aerosol dynamics model by placing them at the corresponding size at the rate given by the nucleation model. This procedure involves the following assumptions:

1. The distribution of the smallest particles below the size at which the particles are introduced in the aerosol dynamics model is neglected. That is, the reduction of vapors and the coagulational growth of larger particles by the smallest particles is omitted.

2. The input formation rate is generally determined for a steady-state situation: it is assumed that the formation rate at a small size immediately adapts to changes in the ambient conditions, such as the concentrations of condensable vapors and scavenging sinks.

METHODS FOR TESTING THE ASSUMPTIONS

The validity of the above-listed assumptions 1 and 2 is tested with a discrete particle population model that simulates the dynamics of ~sub-10 nm particles molecule-by-molecule by solving the particle birth–death equations. We use a simplified model set-up with parameters representative of typical atmospheric molecules involved in new-particle formation (see Olenius and Riipinen, 2017 for more details). The quasi-unary model substance represents particles formed by sulfuric acid-driven initial nucleation, that
grow also by condensation of additional organic compounds from a diameter of \( d_p = 3 \text{ nm} \) upward. We simulate particle formation events for 24 hours for different atmospheric boundary layer environments: representative (a) remote, (b) average, and (c) polluted locations, for which the concentration of the nucleating vapor and the scavenging sink increase from low to high. The vapor concentration follows a sinusoidal diurnal pattern, and the scavenging sink is assumed to remain constant during the simulation.

First, the nanoparticle population from vapor molecules to \( \sim 11 \text{ nm} \) particles is simulated explicitly to yield the “true” result for the particle concentrations and the formation rate at \( 1.5 \text{ nm} \). The assumptions are then tested in the following way:

1. To assess the effect of omitting the smallest particles below the size at which the initial formation rate is determined (here \( 1.5 \text{ nm} \)), the same conditions are simulated again, this time using the time-dependent formation rate \( J_{1.5 \text{ nm}}(t) \) recorded in the explicit simulation as an input. \( J_{1.5 \text{ nm}}(t) \) is used as a source term at \( 1.5 \text{ nm} \), and the birth–death equations are solved only for the vapor molecules and sizes larger than \( 1.5 \text{ nm} \).

2. To evaluate the steady-state assumption, the simulations are run using an input formation rate \( J_{SS,1.5 \text{ nm}} \) at \( 1.5 \text{ nm} \), determined for steady-state situations corresponding to the simulation conditions.

RESULTS

Total concentrations of particles above \( d_p = 1.5, 3, 5 \text{ and } 10 \text{ nm} \) in simulations with and without assumptions 1 and 2 are presented in Figure 1. Omitting the distribution below \( 1.5 \text{ nm} \) (assumption 1; dashed lines in Figure 1) may have a decreasing effect on the modeled nanoparticle concentrations. For the polluted environment, the particle concentrations are underestimated by a factor of \( \sim 0.6 \) when employing the assumption: at high vapor concentrations, the sub-\( 1.5 \text{ nm} \) particles in the explicit simulation are numerous enough for the particles to contribute to the formation and growth of the \( >1.5 \text{ nm} \) sizes by coagulation, and the omission of these processes decreases the simulated particle concentrations. For the remote and average boundary layer conditions, the underestimation is less significant, of a factor of \( \sim 0.9 \), due to lower concentrations of sub-\( 1.5 \text{ nm} \) particles. In general, the effect of assumption 1 is small, but it may be significant, for example, for comparisons of modeled and measured concentrations.

The assumption of a steady-state formation rate (assumption 2; dotted lines in Figure 1), on the other hand, can have more prominent effects on the resulting concentrations of newly formed particles. In this case, the concentrations may become overpredicted by factors between \( \sim 2 \) and 30, depending on the ambient conditions. In the steady-state scheme, the formation rate at \( 1.5 \text{ nm} \) follows the vapor concentration with no delay, while in reality the true time-dependent formation rate may not reach the steady-state value corresponding to the peak vapor concentration before the vapor concentration starts decreasing after the peak. The steady-state assumption becomes bad especially for the remote environment, for which the time scales of condensational growth and scavenging are longer.
Figure 1. Total concentration of small particles larger than $d_p = 1.5, 3, 5$ and $10$ nm in different representative boundary layer conditions for the explicit simulation that gives the exact result (black solid lines), and for simulations with assumptions 1 (red dashed lines; indistinguishable from the solid lines for the remote and average environments) and 2 (red dotted lines). Concentration of the nucleating vapor is also shown for reference in the top panels (blue dash-dotted lines).

CONCLUSIONS

The presented results demonstrate that common assumptions, which are in practice applied in all aerosol dynamics and large-scale models, may cause significant uncertainties in the description of nucleation in new-particle formation modeling. While the omission of the smallest particles below the input size of the aerosol dynamics model may somewhat underpredict the growth of larger particles especially in polluted environments, the assumption of a steady-state formation rate may lead to a notable overprediction of the concentrations of newly formed nanoparticles. More detailed studies are needed to quantify these effects for different atmospheric molecular systems.

ACKNOWLEDGEMENTS

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REFERENCES

Baranizadeh, E. et al. (2016). Implementation of state-of-the-art ternary new-particle formation scheme to the regional chemical transport model PMCAMx-UF in Europe, Geosci. Model Dev. 9, 2741.

DIRECT OBSERVATION OF CLUSTER SIZE DISTRIBUTIONS DURING NUCLEATION AND GROWTH IN LAVAL EXPANSIONS

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Keywords: Nucleation, Cluster-size resolved growth kinetics, Laval nozzle, Photoionization

INTRODUCTION

We have recently (Ferreiro et al., 2015; Ferreiro et al., 2016) reported on fundamental studies of the condensation of propane gas in the uniform (constant pressure and temperature) postnozzle flow of Laval nozzles using soft single-photon ionization by vacuum ultraviolet light and mass spectrometric detection. The whole process, from nucleation to growth of nanosized molecular aggregates (∼10 nm in diameter), can be monitored at the molecular level with a time-resolution of ∼3 µs. We record mass spectra at chosen times, pressures and temperatures which allows us to (i) determine directly the critical nucleus size range as well as (ii) kinetics and possible mechanisms of cluster-size specific growth. Here, we demonstrate results on homogeneous gas phase nucleation of propane and toluene as well as systematic results on growth processes for propane, toluene (Chakrabarty et al., 2017) and water clusters. Additionally, we discuss how information about the size, composition, and abundance of individual molecular clusters provides unique experimental data for comparison with ongoing molecular-level simulations.

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REFERENCES


A NEW PARAMETERIZATION OF INORGANIC NUCLEATION BASED ON MEASUREMENTS FROM THE CERN CLOUD EXPERIMENT

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Keywords: global modelling, nucleation, inorganic nucleation, parameterization.

INTRODUCTION

Nucleation is known to be a significant source of climate-relevant aerosol throughout the atmosphere. However, performing atmospherically relevant nucleation experiments in a laboratory setting is extremely challenging. As a result, until now, the parameterizations used to represent new particle formation in global aerosol models were largely based on in-situ observations or theoretical nucleation models, and usually only represented the binary H$_2$SO$_4$-H$_2$O system.

The CERN CLOUD experiment was designed to provide the most controlled and accurate nucleation rate measurements to date, over the full range of free tropospheric temperatures and down to sulfuric acid concentrations of the order of $10^5$ cm$^{-3}$. Its initial purpose was to investigate the proposed link between galactic cosmic rays and the Earth’s climate (Kirkby, 2007). The focus of the experiment later widened to include inorganic, organic, and amine-driven nucleation.

METHODS

Sulfuric acid is often seen as the driving force behind atmospheric nucleation. However, several different chemicals can affect particle formation rates, even at extremely low trace concentrations which are technically challenging to measure directly. Nucleation rates also respond to environmental changes in e.g. temperature in a highly non-linear fashion. We will present a parameterization of inorganic nucleation rates for use in global models, based on measurements made at the CERN CLOUD chamber. The parameterization includes four separate nucleation pathways: binary neutral, binary ion-induced, ternary neutral, and ternary ion-induced.

This inorganic nucleation parameterization derived from CLOUD measurements has been implemented in the GLOMAP global aerosol model, together with the CLOUD-based organic parameterization of Riccobono et al. (2014). The parameterizations depend on temperature and on concentrations of sulfuric acid, ammonia, organic vapours, and ions.

The atmospheric aerosol system can be saturated with respect to nucleation, meaning that the response of large, climate-relevant particles to any individual pathway will be damped by the contribution of other particle formation mechanisms. As a result, in a present-day atmosphere, the changes in climate-relevant aerosol (in the form of cloud-level cloud condensation nuclei) over a solar cycle are on average about 0.1%, with local changes of less than 1%. In contrast, anthropogenic changes in ammonia since pre-industrial times were estimated to have a much greater influence, resulting in a radiative forcing of between -0.62 and -0.66 W m$^{-2}$. 
CONCLUSIONS

Including ternary inorganic pathways in GLOMAP improved the model’s agreement with free tropospheric observations, especially aircraft measurements. The further inclusion of an organic parameterization, which increased nucleation in the summertime boundary layer, brought our results more in line with observations made at surface stations. We therefore believe that, while the addition of other nucleation pathways (such as amine-induced nucleation) will doubtless improve agreement with local in-situ measurements of total aerosol concentration, this model set-up provides a good representation of the global atmosphere as a whole.

ICNAA is an ideal conference at which to present this parameterization, to encourage its uptake among the global aerosol modelling community.

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REFERENCES

Atmospheric evidence for pure biogenic nucleation

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INTRODUCTION

Atmospheric formation of nanometer sized particles is a frequent phenomenon which significantly contributes to global aerosol particle number concentration throughout the troposphere (Merikanto et al., 2009). It results from a complex sequence of different processes including the production of clusters from gaseous precursors and the growth of these clusters to particles. Besides their effect on human health, these newly formed particles can, after they grow to larger sizes, act as cloud condensation nuclei (CCN), and impact the climate through cloud related radiative processes (Kerminen et al., 2012). Global models predict that new particle formation (NPF) could produce a substantial fraction of the total CCN budget, up to 70% in some regions (Yu and Luo, 2009), and in turn strongly control the present-day climate forcing of aerosol particles.

Benefiting from the continuous advancement of measurement techniques, our understanding of NPF has significantly improved during the last decade. For instance, state-of-the-art mass spectrometers, namely API-TOF (Atmospheric Pressure interface Time-Of-Flight; Junninen et al., 2010) and CI-API-TOF (Chemical Ionization Atmospheric Pressure interface Time-Of-Flight; Jokinen et al., 2012), have provided new insights into the identification of the gaseous precursors involved in the process. Using such techniques, evidence for the role of oxidized organic compounds (referred as HOMs, Highly Oxidized Multifunctional organic compounds) together with sulfuric acid already in the early stages of the NPF process was highlighted in several studies (eg. Bianchi et al., 2016; Ehn et al., 2014; Schobesberger et al., 2013). More recently, Kirkby et al. (2016) reported ion induced cluster formation solely from α-pinene oxidation products under atmospheric conditions in the CERN CLOUD (Cosmics Leaving OUtdoor Droplets) chamber.

Although organic nucleation at extremely low sulphuric acid concentration has been already observed in the free troposphere (Bianchi et al., 2016), the aforementioned mechanism, in which highly oxidized biogenic molecules form new particles, has never been clearly evidenced in the real atmosphere.

METHODS

Measurements were conducted in the boreal SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005), from April-June 2013. “Evening” cluster ion formation events were detected from sub-3 nm negative ion measurements using a BSMA (Balance Scanning Mobility Analyser, 0.8-5 nm; Tammet et al., 2006), with a focus on the 18:00–00:00 local time window, in the light of the recent work by Buenrostro Mazon et al. (2016). In order to avoid any rain related effects in the production of ions, all evenings showing evidence of precipitation after 16:00 were filtered out. The molecular composition of negatively charged ions was resolved with an API-TOF, and the concentrations of neutral gas-phase sulfuric acid and HOMs were measured with a nitrate ion based CI-API-TOF. The calibration of the CI-API-TOF was based on sulfuric acid detection, and the resulting calibration coefficient was assumed to allow also for the determination of HOMs concentration (Jokinen et al., 2012).
Measurement uncertainty is estimated to be in the range -50% to +100%, because of both calibration and transmission related effects.

Additional trace gas and ambient meteorological data, including O₃ (ozone analyser based on the absorption of UV radiation) and NO (chemiluminescence analyser) concentrations, as well as UVB-radiation (SL 501A pyranometer), temperature (PT-100 sensor) and relative humidity, all measured at a mast height of 16.8 m, were included in the analysis. Particle size distributions measured with a Differential Mobility Particle Sizer (DMPS; 3–1000 nm) were finally used to calculate the condensation sink (CS), which describes the loss of vapours on pre-existing particles (Kulmala et al., 2012).

CONCLUSIONS

The formation of negatively charged clusters was frequently observed before the sunset, as illustrated on Figure 1. In addition to low sulfuric concentrations, the simultaneous appearance of HOM dimers and their subsequent “growth” up to tetramers, which is not observed in the absence of cluster ion formation event, suggests a strong involvement of these biogenic compounds in the formation of the negatively charged clusters, as previously shown by Kirkby et al. (2016). Moreover, the cluster formation rates measured in Hyytiälä are similar to those reported from the CLOUD experiment in comparable conditions, supporting the fact that the mechanism evidenced in the chamber might also occur in the real atmosphere. However, since the newly formed clusters do not grow beyond 3 nm in Hyytiälä, the relevance of the ion induced pure biogenic nucleation with respect to climate might be very limited, at least in the boreal forest.

Figure 1. Identification of “evening” negative cluster ion formation events on 20 – 21 April 2013 using BSMA measurements. The events are seen in both nights from ~ 20:00 to midnight (local time) on the surface plot (a) as well as from the increase in cluster ion concentration in two size ranges, 1.4–2 nm and 2–3 nm (b).
REFERENCES


INFLUENCE OF ATMOSPHERIC CONDITIONS ON PURE BIOGENIC NUCLEATION IN THE CLOUD CHAMBER

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INTRODUCTION

Atmospheric aerosols affect both human health (Harrison and Yin, 2000) and Earth’s radiative energy balance, either directly or indirectly via their influence on clouds (IPCC, 2013). New particle formation (NPF) by gas-to-particle conversion forms initial molecular clusters around 1 nm diameter, which then grow by vapour condensation and may reach sizes above around 50 nm, where they can act as cloud condensation nuclei (Kulmala et al., 2013). NPF is estimated to contribute to a substantial fraction of global cloud condensation nuclei (Merikanto et al., 2009; Kerminen et al., 2012). Originally, it was thought that NPF can only occur in the presence of sulfuric acid vapour (Kuang et al., 2008) and that ions do not play a major role (Hirsikko et al., 2011, and references therein). However, chamber and laboratory experiments have shown that particles can form from organic precursors in the absence of sulfuric acid (Zhao et al., 2013; Kirkby et al., 2016). However, the atmospheric relevance in the present day atmosphere is under investigations.

Kirkby et al. (2016) presented evidence for pure biogenic particle formation solely from highly oxidized α-pinene oxidation products under atmospheric conditions in the CERN CLOUD (Cosmics Leaving OUtdoor Droplets) chamber. Kirkby et al. (2016) also showed that ions from galactic cosmic rays enhance the particle formation rates by up to a factor 10-100 in the system investigated in their study. Ion-induced nucleation is therefore the main pathway for the formation of initial clusters from highly oxygenated molecules (HOMs) resulting from ozonolysis of biogenic vapours. Pure biogenic nucleation may help understand night-time NPF (Buenrostro Mazon et al. 2016), which occurs in the absence of sulfuric acid, and also NPF in very clean environments such as rain forests or at high altitudes (Bianchi et al. 2016). Furthermore, ion-induced pure biogenic nucleation appears to have been the dominant mechanism for NPF in the pristine pre-industrial climate (Gordon et al., 2016).

The discovery of pure biogenic nucleation reported by Kirkby et al. (2016) resulted from ozonolysis of a single monoterpenic (α-pinene) at 5°C and in the absence of other vapours. Here we report pure biogenic nucleation rates measured in the CLOUD chamber in 2015 and 2016, and extend the original study to include several biogenic vapours - monoterpenes, sesquiterpenes and isoprene - under a range of environmental conditions (NOx, ion concentrations, relative humidity, daytime/nighttime conditions and temperature). Our aim is to study the influence of a more realistic atmospheric conditions on pure biogenic nucleation.
METHODS

The CLOUD experiment at CERN (Kirkby et al., 2011; Duplissy et al., 2016; Kirkby et al., 2016) is designed to study particle formation under extremely low contamination levels and precisely controlled conditions. The 3-m-diameter stainless-steel chamber enables a detailed investigation of the effects of cosmic rays on aerosols, cloud droplets and ice particles under atmospheric conditions. The large volume (26.1 m³) and dual internal mixing fans result in homogeneous and highly stable operating settings. The CLOUD chamber has an advanced gas system that maintains stable precursor gas concentrations in the desired 1 pptv – 10 ppbv range. To maintain low contamination, the electro-polished chamber walls are periodically cleaned with ultra-pure water and then heated to 100°C during a cleaning cycle that lasts between 1 and 3 days. To further minimize contaminants, the chamber is supplied with synthetic air from evaporation of liquid nitrogen and liquid oxygen, mixed in the ratio 79:21. Ozone is introduced into the chamber, normally in the range of 10-40 ppbv, but as high as 1 ppmv when a cleaning cycle is in progress in order to help remove organic contaminants.

The accurate control of the chamber properties along with its high cleanliness allows particle formation to be studied under atmospherically relevant conditions. Moreover, the chamber can be exposed to a pion beam from the CERN Proton Synchrotron to allow the control of the ion-pair concentrations in the chamber between ground level and the lower stratosphere. Furthermore, the chamber is equipped with high voltage electrodes for creating an ion-free environment and measuring so-called “neutral” (uncharged) nucleation. By subtracting the neutral nucleation rate from the GCR or pion beam rates, the ion-induced nucleation rate can be determined.

The new measurements to be reported here were made during the CLOUD10 (September to December 2015) and CLOUD11 (September to November 2016) campaigns. The experiments started with different concentrations of pure monoterpene (α-pinene and δ-3-carene, individually and then as a mixture) at different temperatures (-25, 5, 25 °C). In later experiments, a sesquiterpene (β-caryophyllene) and isoprene were studied both individually and in a pure biogenic “soup” together with monoterpenes (α-pinene). The nucleation rates resulting from the oxidation of the mixture under varying conditions were measured. Different atmospheric environments were simulated in the CLOUD chamber by varying the NOx concentration (and its photolysis rate), UV irradiation, ion concentration (neutral vs. ion-induced nucleation), relative humidity (0-80%) and temperature (-35 to 25 °C). An example of pure biogenic particle formation from a soup of α-pinene, isoprene and β-caryophyllene at 5 °C is shown in Figure 1. Upon increasing the concentrations of the individual components of the mixture, an increase in nucleation and growth rates is evident. The size distribution was measured with three instruments, a scanning PSM (Vanhanen et al. 2011), a DMA-train (Stolzenburg et al. 2016) and a TSI nano-SMPS (Wang and Flagan 1990).

CONCLUSIONS

Biogenic vapours alone can form particles at rates comparable to sulfuric acid – ammonia/DMA systems under low-pollution conditions. During the CLOUD10 and CLOUD11 campaigns we carried out the first study of the effect of different atmospheric conditions on pure biogenic nucleation using an atmospherically-relevant mixture of monoterpenes, a sesquiterpene and isoprene. In particular, we studied the effect of NOx on the pure biogenic nucleation rates under night-time and daytime conditions, which modifies the properties of extremely low volatility organic compounds (ELVOCs) – the subset of HOMs that are mainly responsible for particle nucleation.

The well-controlled, low contamination CLOUD chamber at CERN has enabled us to perform a wide-range of experiments on pure biogenic nucleation under realistic atmospheric conditions. We are able present a first picture of pure biogenic nucleation under conditions corresponding to night-time boreal forests, NOx-polluted forested regions, tropical rain forests at low and high altitudes, and the pristine pre-industrial climate.
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REFERENCES


Gordon, Hamish, Kamalika Sengupta, Alexandru Rap, Jonathan Duplissy, Carla Frege, Christina Williamson, Martin Heinritzi, Mario Simon, Chao Yan, and João Almeida (2016). "Reduced Anthropogenic Aerosol Radiative Forcing...


Poster Session I

1. Gerald Wilemski: Wetting transitions in alkane-water nanodroplets
2. Angela Buchholz: The effect of relative humidity and chemical composition on the evaporation of SOA particles
3. Roope Halonen: Molecular dynamics and isothermal homogeneous nucleation
4. Jonathan Barrett: Tolman length and rigidity constants for the hard-core Yukawa fluid
5. Michael Anisimov: Impact of phase transitions in condensed phases on the geometry of vapor nucleation rate surfaces
6. Sergey Valiulin: Mechanism of formation and explosibility of the organic nanoaerosol in coal mines
7. Evgeni Zapadinsky: Non-equilibrium cluster properties and non-isothermal nucleation
8. Victor Kurasov: Metastable phase decay at the decreasing rate of growth
11. Daniel Schlesinger: Water accommodation on ice
13. Sho Ayuba: Kinetic analysis of homogeneous droplet nucleation using large scale molecular dynamics simulation
15. Ricky Teiwes: A new setup for the study of ion-molecule and ion-photon reactions relevant for aerosol science

16. Mikko Äijälä: Exploratory classification of aerosol mass spectra

17. Martta Toivola: Computational prediction of salting in and salting out effects

18. Craig Stroud: The effect of particle acidity on a-pinene SOA formation

19. Dimitri Castaréde: A thermodynamic description for the continuous deliquescence of atmospheric aerosol particles

20. Julian Thompson: Work of formation of Caesium Hydroxide clusters determined by guided mitosis

21. Egon Tschurtschenthaler: Controlling nucleation rates with patterns of impurities

22. Janne Lampilahti: Boundary layer new-particle formation and roll vortices

23. Liqing Hao: Combined effects of boundary layer dynamics and atmospheric chemistry on aerosol composition during new particle formation periods

24. Lubna Dada: Method for identifying NPF types using characteristic nucleation-mode particles and ions


26. Ricardo Morales: Temperature dependence of particle number concentration produced by a two stroke engine

27. Heikki Lihavainen: New particle formation at rural background site in Western Saudi Arabia


29. Juha Sulo: Observed differences between event and non-event days in levels of amine and ammonia containing comp

30. Erik Thomson: Observations of a diurnal cycle of ice nucleating particle concentration on the shoulders of Mt. Kenya

31. Thomas Koop: Ice nucleation and antifreeze properties of biological macromolecules

32. Jiun-Horng Tsai: Airborne PM2.5 concentration improvement under various control scenarios – a case study in Taiwan
33. Zoltán Németh: Multi-year long new particle formation in urban environments
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40. Chin-Hsiang Luo: Impact of regional microclimate and PM2.5 concentration on sub-urban atmospheric visibility
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44. Juergen Spielvogel: A candidate measurement system for the standardized routine monitoring of particle number concentration
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47. Kristina Höhler: Ice nucleation activity of arable soil dust aerosol particles
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50. Ilona Ylivinkka: Estimation of the CO2-induced terrestrial climate feedback in subarctic region
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WETTING TRANSITIONS IN ALKANE-WATER NANODROPLETS

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Keywords: Nanodroplets, Wetting, Droplet Morphology, MD Simulations.

INTRODUCTION

Interest in the morphology of liquid-liquid phase separated aerosol droplets has grown considerably over the past 20 years. Qiu and Molinero, (2015) present a large list of experimental and theoretical investigations that have helped to advance our understanding of this subject. Most of these prior investigations have focused on the effects of droplet composition and relative humidity on droplet morphology at a single temperature. In contrast, our efforts have used molecular dynamics simulations to study the temperature dependent wetting behavior of nonane-water nanodroplets and its influence on droplet structure. We use the SPC/E water model and a unified atom 6-12 Lennard-Jones (LJ) model for alkanes. Water-alkane interactions are treated using a LJ potential with energy and size parameters adjusted to reproduce experimentally observed wetting behavior for nonane at 295 K. For reasonable values of the LJ parameters, core-shell structures of nonane-water nanodroplets are observed at low temperatures, $T < 235$ K, indicating that nonane perfectly wets supercooled SPC/E water with a zero contact angle at low temperatures. At higher $T$, imperfect wetting is found as a nonane lens forms on the water drop with a finite, non-zero contact angle yielding a partially engulfed Russian Doll structure. We also studied planar alkane-water interfaces. For these systems, our simulation results are consistent with the occurrence of low temperature and high temperature wetting transitions. Within the imperfect wetting region at low temperature, the contact angle formed by alkanes on water initially increases with temperature until a maximum dewetting temperature (MDT) is reached. Beyond the MDT, the contact angle decreases as the system approaches the usual high temperature wetting transition.

COMPUTATIONAL MODELS AND METHODS

All simulations were performed with either the GROMACS (Berendsen et al., 1995; Hess et al., 2008) or LAMMPS (Plimpton, 1995) molecular dynamics simulation packages. Long time simulations of 10-50 ns were carried out using the (NVT) canonical ensemble with periodic boundary conditions and a time step of 2 fs. The Nosé-Hoover algorithms (Nosé, 1984a, 1984b; Hoover, 1985) were used to control the system temperature with a coupling time constant of 0.2 ps. Water was treated with the SPC/E potential (Berendsen et al., 1987) Methyl and methylene groups of the alkanes were treated in the united atom approximation. All short-range intermolecular interactions were handled with Lennard-Jones (LJ) potentials with a cut-off radius of 1.5 nm. The long-range coulomb interaction between water molecules was also cut-off at 1.5 nm. Both of the short-range and long-range interactions were handled with twin-range cutoffs and the neighbor list was updated every fifth time step (10 fs). For the alkane models, we used force field parameters from Yi and Rutledge (2009). In our earlier work (Hrahsheh and Wilemski, 2013), we used the geometric mean combining rule to determine the LJ parameters ($\epsilon/\sigma$) between unlike atoms, but these values produced much larger contact angles for nonane drops on water compared to thermodynamic estimates using the best measured values for the nonane-water interfacial tension (Goebel and Lunkenheimer, 1997). Because our simulated surface tensions for pure water and nonane are
systematically somewhat lower than the experimental values, we chose to adjust the \((\varepsilon, \sigma)\) values not to fit the measured nonane-water interfacial tension, but rather to approximate the spreading coefficient \(S\) for nonane (N) on water (W). The spreading coefficient is defined as the following difference of interfacial tensions \(\gamma\), \(S = \gamma_W - (\gamma_N + \gamma_{NW})\). While adjusting the \((\varepsilon, \sigma)\) values, we discovered that the simulated contact angles were rather sensitive to small changes in either parameter. A similar observation has been reported by Qiu and Molinero (2015). In addition to the nanodroplet simulations, we also performed many simulations of alkane-water planar interfaces. Two types of planar simulation systems were used: (1) liquid (alkane or water) slab inserted in vapor and (2) a slab of water sandwiched between a pair of identical alkane slabs surrounded by vapor. From these simulations, the interfacial tensions for liquid-vapor and liquid-liquid interfaces could be determined. These values could then be used with the rigorous thermodynamic formula, (Rowlinson and Widom, 1982)

\[
\cos \theta = \frac{\gamma_W^2 - (\gamma_N^2 + \gamma_{NW}^2)}{2\gamma_N \gamma_{NW}}
\]

to calculate the contact angle \(\theta\). Similar values of \(\theta\) would also be obtained from the simpler Young’s equation, as shown by Qiu and Molinero (2015).

RESULTS AND CONCLUSIONS

Nonane-water nanodroplets containing 1000 water molecules and 500 nonane molecules were simulated at \(T = 230\) K and 295 K using the adjusted cross interaction parameters \(\varepsilon = 0.65\) kJ/mol and \(\sigma = 0.362\) nm. For comparison, the values used in our earlier simulations were \(\varepsilon = 0.55\) kJ/mol and \(\sigma = 0.359\) nm. Snapshots of cross-sections of the simulated nanodroplets are shown in Fig. 1. The low temperature droplet clearly has a core-shell structure indicative of perfect wetting with a contact angle of 0°. In contrast, the higher temperature droplet has assumed a Russian doll structure characteristic of imperfect wetting. The nonane lens has a nonzero contact angle on water.

Figure 1. Cross-sectional snapshots of simulated water (blue) and nonane (yellow) nanodroplets at \(T = 230\) K (left) and \(T = 295\) K (right). The core-shell structure is evident on the left, while the warmer droplet on the right has a Russian doll structure characteristic of imperfect wetting.
The occurrence of perfect wetting at low temperatures is consistent with the unusual behavior found previously by Hrahsheh and Wilenski (2013) in which $\theta$ increased with $T$. We explored this further by calculating $\theta$ from interfacial tensions obtained from simulations of planar bulk interfaces using cross interaction parameters $\epsilon = 0.65 \text{ kJ/mol}$ and $\sigma = 0.359 \text{ nm}$. The results obtained so far for nonane and water are shown in Figure 2.

![nonane-water](image)

**Figure 2.** Temperature dependence of the nonane-water contact angle found from MD simulations of planar bulk interfaces. Two sets of results are shown: The older results of Hrahsheh were found using GROMACS; the newer results of Neupane (with error bars) were obtained with LAMMPS. The two sets are in good agreement. The solid line is based on fits to the simulated interfacial tensions.

Calculated contact angles are quite sensitive to small fluctuations in the simulated values of the interfacial tensions. To reduce this sensitivity, we also calculated $\theta$ using fits to the simulated interfacial tensions. This results in a much smoother variation of $\theta$ with $T$, as can be seen in Figure 2. Using the fitted surface tensions, the calculated contact angles show that both an upper and lower wetting transition temperature occurs for the nonane-water and octane-water (not shown here) systems. In contrast to conventional expectations, the simulated contact angles formed by octane and nonane on water at low temperature ($T=250\text{K}$) tend to increase with temperature until reaching a maximum dewetting temperature (MDT). Similar behavior was observed in nonane-water nanodroplet simulations but only at low $T (< 300 \text{ K})$ where droplet simulations can be performed. For the planar systems, after the MDT is passed, the contact angle decreases, as expected, until perfect wetting is achieved at a higher temperature. Although lower wetting transition temperatures have been reported for partially miscible liquids with lower consolute points, the presence of a low-$T$ wetting transition in the essentially immiscible alkane-water systems is highly unusual and has not been reported before. In future work, we will explore whether this low-$T$ wetting transition is found only for the SPC/E water model or if it occurs for other popular models such as TIP5P (Mahoney and Jorgensen, 2000) or monatomic water (Molinero and Moore, 2009).

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REFERENCES

dynamics with coupling to an external bath, J. Chem.Phys. 81, 3684.
potentials, J. Phys. Chem. 91, 6269.
parallel molecular dynamics implementation, Comp. Phys. Comm. 91, 43.
369.
1695.
Hrahshheh, F. and G. Wilemski (2013). Fluctuating structure of aqueous organic nanodroplets, in
Mahoney, M.W. and W. L. Jorgensen (2000). A five-site model for liquid water and the reproduction of
Molinero, V. and E. B. Moore (2009). Water modeled as an intermediate element between carbon and
Chem. Phys. 81, 511.
52, 255.
137, 10642.
York, N.Y.), p. 211.
Phys. 131, 134902.
THE EFFECT OF RELATIVE HUMIDITY AND CHEMICAL COMPOSITION ON THE EVAPORATION OF SECONDARY ORGANIC AEROSOL PARTICLES

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Keywords: evaporation, volatility, secondary organic aerosol, chemical composition.

INTRODUCTION

Secondary Organic Aerosol (SOA) is a major constituent of atmospheric aerosol. SOA consists of a multitude of organic compounds with a wide range of physical and chemical properties, such as viscosity and volatility (Hallquist et al., 2009). The volatility and concentration of a compound will determine its partitioning between particle and gas phase. One approach to characterize the composition of SOA particles is the Volatility Basis Set (VBS) model (Donahue et al. 2006) where compounds are grouped by their saturation concentration. Typically, VBS distributions are derived from particle growth experiments in smog chambers, and can then be used to predict various SOA properties, including the rate of evaporation of SOA particles upon dilution of aerosol with clean air. Previous studies have shown that the evaporation of α-pinene ozonolysis SOA particles in the presence of an irreversible sink for organic vapors is slower than expected from their VBS distributions (Vaden et al. 2011). The observations were explained by hindered diffusion of SOA compounds within the particles, consistent with the observation that α-pinene ozonolysis SOA particles are amorphous solids (Virtanen et al. 2010).

Another way to study the volatility of SOA compounds is to track the equilibrium particle size as well as composition as a function of temperature. These experiments are typically carried out with thermo-denuders. However, the possibility of accelerated chemical reactions occurring in heated particles complicates the interpretation of the thermodenuder experiments.

We studied the evaporation behavior of SOA particles produced from α-pinene and complex VOC mixtures at different oxidation levels. Unlike studies with thermo-denuders we investigated the evaporation of the particles at room temperature in a residence time chamber (RTC) therefore eliminating thermal decomposition artefacts. We also investigated the impact of relative humidity (RH) on the particle evaporation.

Besides the physical mass transfer limitations in (semi)solid particles, there may also be chemical processes at work in the particle phase, e.g., oligomerization reactions, decreasing the rate of evaporation of the particles. Thus, studying the changes of the chemical composition of particles during evaporation may provide further insights into the processes governing the particle evaporation kinetics. Therefore, the chemical composition of the particles was investigated with two complementary methods: Aerosol Mass Spectrometry, which provides an average atomic composition of SOA particles, and a Filter Inlet for Gases and Aerosols (FIGAERO) coupled with Chemical Ionization Time-of-Flight Mass Spectrometer (CIMS) which provides information on molecular composition as well as volatility of the compounds.
METHODS

An Aerodyne Potential Aerosol Mass (PAM) oxidation flow reactor (Lambe et al., 2011) was used to produce SOA with a range of compositions via photooxidation of α-pinene or a complex mixture of VOCs. For all experiments, the basic conditions in PAM were constant (residence time, RH, temperature, initial VOC concentration). The integrated oxidant exposure inside the reactor was manipulated by varying the UV light intensity, thereby allowing the generation of SOA with O:C ratios ranging from 0.55 – 1.05. A Nano-Differential Mobility Analyzer (NanoDMA 3085, TSI Inc.) was used to select a quasi-monodisperse particle distribution at 80nm. The NanoDMA also removed the majority of gas phase compounds due to the extremely short residence time and the open loop configuration of the sheath flow (dilution factor ~100). The changes in particle size and composition were measured with a set of instruments (see below). The length of the stainless steel tubing leading to these instruments was varied to achieve evaporation times between 4 and 150 sec. To investigate evaporation times up to 10 h, the monodisperse aerosol was flushed into the 100 L stainless steel residence time chamber (RTC) and then the RTC was closed off from all air flows. The content was sampled briefly in ~1 h intervals replacing the sampled volume with clean air. The stainless steel surfaces of the tubes and the RTC acted as an irreversible sink for the vapors evaporating off the particles, as confirmed by the insensitivity of the observed particle evaporation rates to the initial particle concentrations in the system. A second set of experiments was conducted with longer RTC filling times in order to reach the higher aerosol mass concentrations needed for FIGAERO measurements. Two to three hours after ending the filling, the content of the RTC was sampled onto the FIGAERO filter and analyzed.

For the humid experiments (RH 40% & 80%), the RH of the system was controlled by humidifying the sheath flow of the size selection NanoDMA while maintain constant humidity inside the PAM reactor. The RTC was flushed with air of the target RH prior to the experiments.

The VOC concentration on the inlet of the PAM was measured with a Proton Transfer Reaction time-of-flight Mass Spectrometer (PTRMS, Ionicon).

The chemical composition of the SOA particles was investigated with a High Resolution time-of-flight Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc.) and a Filter Inlet for Gases and AEROsols (FiGAERO, Aerodyne Research Inc., Lopez-Hilfiker et al., 2014) coupled with Chemical Ionization Time-of-Flight Mass Spectrometer (ToF-CIMS, Aerodyne Research Inc. and ToFwerk AG) using iodide-adduct ionization (Lee et al., 2014). The size distribution of the particles was measured with a Scanning Mobility Particle Sizer (SMPS, TSI Inc.). RH and T were monitored with Humicap sensors (Vaisala).

Figure 1: Schematic diagram of the experimental set-up. White circles indicate valves that switch between bypass lines and size selection (DMA)/Residence Time Chamber (RTC).
RESULTS AND DISCUSSION

Results from a typical experiment are shown in Figure 2. Particles evaporated already during the short passage from the NanoDMA to the SMPS (up to 5% reduction of particle diameter). After further fast evaporation during the first ~30 min in the RTC, the diameter continued to decrease slowly as the particles were sitting in the RTC for several hours. Although the particle evaporation considerably reduced the particle size, the O:C ratio measured by the AMS was stable throughout each evaporation experiment. But there was a clear dependence of the observed evaporation rate on the initial chemical composition of the SOA, as expressed by the O:C ratio, with volatility and the evaporation rate increasing with decreasing O:C ratio.

![Figure 2](image1.png)

Figure 2. Results from a typical \(D\)-SLQHQH%GURZWK%IDFWRU3%SDUWLFOH%VL\]H%PHDVXUHG%DIWHU%WKH%57&%GLYLGHG%by selected particle size. The grey shaded area indicates RTC filling period. X-error bars indicate the measurement interval, y-error bars are 1 \(\sigma\)-standard deviation from averaging over several measurements.

![Figure 3](image2.png)

Figure 3. FIGAERO Thermogram of fresh SOA sampled directly after size selection (blue) and aged SOA with averaged residence time in the RTC of 3:00 (red).

The FIGAERO measurements (Figure 3) showed a small shift to higher evaporation temperatures for SOA that has aged in the RTC compared to fresh SOA which indicates the removal of more volatile compounds. This suggests that the particles consist most likely of a mixture of more volatile monomers and less volatile dimers which have very similar O:C ratios. Thus, the evaporation of the more volatile compounds does not lead to a considerable change in measured O:C ratio. We found that particles show considerably more evaporation under humid conditions in the RTC compared to dry conditions which is consistent with observations of Wilson et al (2015) and Yli-Juuti et al. (2017) for SOA particles from ozonolysis of \(D\)-pinene. There are two likely explanations: Water acts as a plasticizer thus reducing mass transport limitations in the humidified particles compared to the (semi)solid dry particles, or water can play a more active chemical role for example by hydrolysis of less
volatile dimers resulting in more volatile monomers in the particle phase. The detailed FIGAERO mass spectra will help investigating these two possibilities.

Results of this study have several important implications. Biogenic SOA particles can be transported over long distances from the point of their formation. They are slowly oxidized during the transport, and become more resistant to evaporation during dilution of the transported air mass. Furthermore, the transported air mass can experience changes in temperature and relative humidity, both of which affect the particle evaporation rates. The hindered evaporation may increase climate effect of SOA relative to what would be predicted by an equilibrium gas-particle partitioning model.

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REFERENCES


MOLECULAR DYNAMICS SIMULATIONS AND ISOTHERMAL HOMOGENEOUS NUCLEATION

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Keywords: HOMOGENEOUS NUCLEATION, MONTE CARLO, MOLECULAR DYNAMICS, LENNARD-JONES, CLUSTER.

INTRODUCTION

Two distinct molecular simulation techniques are usually used to predict the nucleation rates: Monte Carlo (MC) and molecular dynamics (MD) simulations. In MD the Newtonian equations of motion of interacting atoms or molecules are solved and hence the method allows directly the study of time-dependent cluster formation. In MC approach a thermodynamic property (in our case the work of cluster formation) is calculated by configurational sampling under some thermodynamic constraints. Using MC we obtain fully isothermal nucleation rate. Whereas in MD nucleation studies even applying thermostats do not bring system to completely isothermal conditions (Wedekind et al., 2007; Toxvaerd, 2016). In this study we compare the nucleation rates obtained with these two different approaches using Lennard-Jones interatomic potential.

METHODS AND RESULTS

The homogeneous nucleation process is directly observed in the large-scale molecular dynamics (MD) simulation procedure presented by Tanaka et al. (2011). Here the system is thermostatted with velocity scaling method, yet the cluster energy distribution deviates from the one corresponding to ambient temperature (Angélil et al., 2014; Wedekind et al., 2007; Toxvaerd, 2016). Influence of different thermostats on nucleation rate has been studied by Wedekind et al. (2007). The different thermostats appeared to affect similarly the nucleation rate except in the simulations with carrier gas as a coolant. Using nonisothermal nucleation theory they also extrapolated these results to higher concentration of the carrier gas when the completely isothermal conditions can be expected.

Contra MD, to calculate the nucleation rates via MC the time-independent results are supplemented to a classical treatment of cluster population dynamics. The classical kinetic model for the steady state nucleation rate can be expressed as the Becker-Döring sum

\[ J = \left[ \sum_{i=1}^{\pi} \frac{1}{\beta_i N_i^{\text{eq}}} \right]^{-1}, \]  

where \( \pi \) is larger than the critical cluster \( n^* \) (McDonald, 1963), \( \beta_i \) condensation rate of \( i \)-cluster and \( N_i^{\text{eq}} \) is the equilibrium cluster concentration determined as

\[ N_i^{\text{eq}} = N_i^{\text{eqi}} \exp \left( -\frac{\Delta W_i}{kT} \right). \]  

The work of cluster formation \( \Delta W_i \) is calculated by semigrand canonical Metropolis Monte Carlo method (Merikanto et al., 2004; Vehkamäki and Ford, 2000; Lauri et al., 2006). In the method
the grand canonical growth and decay probabilities are calculated for a single cluster at the time and the cluster configuration space is traced out in a canonical Metropolis simulation. The average growth and decay probabilities, \( G_i \) and \( D_i \), gained from the simulation have direct relation between the condensation and evaporation rates in the Becker-Döring kinetic scheme and thus we can write the work of formation of an \( i \)-cluster as

\[
\Delta W_i = -kT \sum_{j=2}^{i} \ln \frac{G_{j-1}}{D_j}.
\]

(3)

The MC simulation results can be easily scaled to obtain the work of formation at some other monomer density, so for each temperature the simulation has to be performed only once. For MC and MD to be comparable, we used identical Lennard-Jones potential and cluster connectivity distances.

To obtain the condensation rates, the collision cross section between the cluster and the monomer is geometrically estimated by a simple brute-force Monte Carlo method instead of approximating the clusters as spherical objects with bulk liquid density. Furthermore, the monomer depletion has to be taken into account because about 1% to 40% of the molecules are clustered in the quasi-steady state of MD simulations. So, the unbalanced steady state in calculations with MC data is driven to match the total number density of the MD simulations.

Figure 1: Difference between the nucleation rates obtained by the MC and the MD simulations as a function of the monomer density. The colored circles present the comparison with the MD results by Tanaka et al. (2011) and Diemand et al. (2013). The arrows indicate cases where only the upper limit for nucleation rate was derived. Black symbols shows the comparison with Wedekind et al. (2007). Black squares and a circle refer to MD simulations with velocity scaling thermostat with different time steps \( \Delta t \). Crosses mark the comparison with the nonisothermal nucleation theory.
The results of the comparison are presented in Figure 1. Most of the MD results demonstrate about 1–3 orders of magnitude lower nucleation rates than the ones obtained by MC simulations. Discrepancy between MC and MD with using velocity scaling thermostats is bigger for lower nucleating vapour concentrations and lower temperatures. There is good agreement of MC results with the points obtained by extrapolation to high carrier gas concentrations of MD results by Wedekind et al. (2007).

CONCLUSIONS

Application of MC simulation to nucleation studies implies the validity of the kinetic scheme and using such thermodynamic properties like free energy for small quasi-stable clusters. MD simulations are free from these assumptions even if the kinetic equation is used to calculate the nucleation rate. In that sense MD simulations can be considered as a "numerical experiment", which can confirm or deny a theory. There is good agreement between theory and "experimental" points plotted as crosses, and we know that these points correspond to fully isothermal nucleation. For other points we have clear disagreement between MD and MC results. It has been mentioned (Yasuoka and Matsumoto, 1998; Wedekind et al., 2007) that usage of thermostats in MD simulations related to nucleation problems brings uncertain degree of thermalization. Our results support this idea. This problem grows with lowering down the nucleating vapour concentrations i.e. with approaching to real experimental conditions. The only known option is to use carrier gas as a thermostat in MD simulations studies of nucleation.

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REFERENCES


TOLMAN LENGTH AND RIGIDITY COSTANTS FOR THE HARD-CORE YUKAWA FLUID

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Keywords: Nucleation, Density Functional Theory, Surface Tension, Tolman Length.

INTRODUCTION

Classical density functional theory has proved to be a very popular approach to determining thermodynamic properties of small clusters for use in nucleation theories. The simplest approaches, the squared gradient approximation (SGA) and mean field theory, seem to give the correct qualitative behaviour for simple fluids, although their quantitative accuracy is unclear. Early work indicated a significant difference between these two approaches, but more recent calculations for the cut-off Lennard-Jones fluid showed that the SGA gave values for the planar surface tension that agreed with computer simulations when used with an accurate equation of state (Lutsko, 2011). Here the SGA and a mean field-type approximation are compared to an approach based on the first order mean spherical approximation (FMSA) for the hard-core Yukawa fluid.

METHODS

According to Tang (2005), the free energy of a non-uniform fluid can be approximated by,

\[ F[\rho] = \int d\mathbf{r} \left[ f(\rho(\mathbf{r})) - \frac{1}{2} kT \int d\mathbf{r}_1 c_b(\mathbf{r}_1 - \mathbf{r}_2) \left( \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) - \rho(\mathbf{r}_1)^2 \right) \right], \]

where \( f \) is the free energy of a uniform fluid of density \( \rho \), \( k \) is Boltzmann’s constant, \( T \) is the temperature, and \( c_b \) is the direct correlation function of the bulk fluid at an appropriately chosen density. The precise density to use in evaluating \( c_b \) is unclear but, following Tang, it will be assumed here that the density is constant, with a value to be discussed below. The Euler-Lagrange equation that determines the density profile is then,

\[ f'(\rho(\mathbf{r})) + \alpha \rho(\mathbf{r}) = \mu + kT \int d\mathbf{r}_1 c_b(\mathbf{r}_1 - \mathbf{r}_2) \rho(\mathbf{r}_2), \]

where, \( \mu \) is the chemical potential, \( \alpha = kT \int d\mathbf{r} c_b(\mathbf{r}) \) and the prime denotes differentiation with respect to \( \rho \). Equation (2) is solved for the hard-core Yukawa fluid, with interaction potential,

\[ u(r) = \frac{-\varepsilon e^{-\lambda (r/d - 1)}}{(r/d)} \quad r > d, \]
\[ = \infty \quad r < d, \]

where \( d \) is the hard-sphere diameter and \( \varepsilon \) and \( \lambda \) are the attractive potential parameters. Tang’s (2004) FMSA expression (together with the Carnahan-Starling form for the hard-sphere part) is used for the free energy of the uniform fluid, and three approximations for \( c_b \) were considered: (i) the FMSA correlation function given by Tang (2005), (ii) the SGA, where \( kTc_b \) is approximated by \( (\alpha + m\overline{\nabla^2}) \delta(\mathbf{r}_1 - \mathbf{r}_2) \), with \( m = \frac{1}{\pi} kT \int d\mathbf{r} r^2 c_b(\mathbf{r}) \), and (iii) a Yukawa approximation (YA), where \( kTc_b \) is approximated by a Yukawa form for all \( r \) (not just \( r > d \)), chosen to give the same \( \alpha \) and \( m \) as the FMSA \( c_b \), i.e.

\[ kTc_b = \alpha^2 \exp\left(-\sqrt{\alpha/m} r\right)/(4\pi mr) \quad \forall r > 0. \]
parameters \(a\) and \(m\) are determined using the FMSA expression for \(c_0\). In the SGA, the Euler-Lagrange equation becomes a second order differential equation for \(\rho\):

\[
m
V^2 \rho = f'(\rho(r)) - \mu .
\]

Furthermore, in the YA, applying the operator \(\nabla^2\) to the Euler Lagrange equation gives the following equation for \(\xi(\rho) \equiv f'(\rho(r)) + \alpha \rho(r)\):

\[
m \nabla^2 \xi = \alpha(\xi - \mu - \alpha \xi),
\]

where \(\rho(\xi)\) is found by numerically inverting \(\xi(\rho)\). Thus, both the SGA and YA involve solving a differential equation for the density profile, which is simpler than solving the integral equation in the FMSA.

The surface tension, \(\gamma\), of a spherical droplet of radius \(R\) can be expanded in powers of \(R^{-1}\) as:

\[
\gamma(R) = \gamma_0 - \frac{2 \gamma_0 \delta}{R} + \frac{2k + \bar{k}}{R^2} + ...
\]

Where \(\gamma_0\) is the planar surface tension, \(\delta\) is the Tolman length (in the planar limit) and \(k\) and \(\bar{k}\) are the rigidity constants of bending and that associated with Gaussian curvature, respectively. The rigidity constants depend on the precise definition of \(R\) (Barrett, 2008): here the equimolar dividing surface is used and the associated rigidity constants are indicated by a subscript “e.” Expressions for \(\gamma_0\), \(\delta\), and \(2k + \bar{k}\) are given by Barrett (2008) and by Blokhuys and van Giessen (2013). In the SGA (and hence also the YA, by straightforward substitutions), the expressions given by Wilhelmsen et al. (2015) can be used. All these expressions involve the planar profile, \(\rho(x)\) and, in the case of \(k\), the first order (in powers of \(R^{-1}\)) correction to it, \(\rho_1(x)\), both of which can be found from the relevant Euler-Lagrange equation (Eq. (2), (4) or (5)): see Blokhuys and van Giessen (2013) for more details.

RESULTS

Calculations were performed for the Yukawa fluid with \(\lambda=1.8\). Quantities were made dimensionless using the appropriate combinations of \(d\) and \(\varepsilon\). Tang (2005) suggested using the average of the equilibrium liquid and vapour densities (\(\rho_l\) and \(\rho_v\), respectively) to evaluate \(c_0\). However, it was found that this did not lead to converged solutions for the Yukawa fluid. A similar problem was noted by Lutsko (2007) for the Lennard-Jones fluid, but at higher densities. Here \(c_0\) was evaluated at a density of 0.3\(\rho_c\) values were insensitive to the density used in the range 0.2\(\rho_c\) to 0.4\(\rho_c\). Figure 1 shows the variation of the planar surface tension with temperature. The three approaches give similar results, with the SGA giving the largest values and the YA giving the smallest. However, all approaches overestimate \(\gamma_0\) compared to the molecular dynamics results of González-Melchor et al. (2001). Figures 2 and 3 show the Tolman length and rigidity constants, respectively. Once again, the SGA and YA values bracket the FMSA values.

CONCLUSIONS

Both the SGA and the YA give reasonable agreement with the FMSA for the surface tension, Tolman length and rigidity constants of the liquid-vapour interface in the non-uniform Yukawa fluid, provided the same equation of state is used in all approximations. However, for the surface tension, agreement with molecular dynamics results is less good than that found by Fu and Wu (2004), using a more complicated density functional. It would be of interest to compare the YA with alternative approaches for other fluids such as the Lennard-Jones fluid.
Figure 1: scaled surface tension $\gamma^* = \gamma \sigma d^2 / \varepsilon$ vs scaled temperature $T^* = kT / \varepsilon$ for the hard core Yukawa fluid from the FMSA (solid line), the SGA (dotted line) and the YA (dashed line). The triangles show the molecular dynamics results of González-Melchor et al. (2001).

Figure 2: scaled Tolman length $\delta^* = \delta / d$ vs scaled temperature $T^* = kT / \varepsilon$ for the hard core Yukawa fluid from the FMSA (solid line), the SGA (dotted line) and the YA (dashed line).
Figure 3: scaled rigidity constants,\( (2k_B^* + \overline{k}_c^*) = (2k_B + \overline{k}_c)/\epsilon \), vs scaled temperature \( T^* = kT/\epsilon \) for the hard core Yukawa fluid from the FMSA (solid line), the SGA (dotted line) and the YA (dashed line).

REFERENCES


IMPACT OF PHASE TRANSITIONS IN CONDENSED PHASES ON THE
GEOMETRY OF VAPOR NUCLEATION RATE SURFACES

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Keywords: nucleation, phase transitions, phase equilibria diagrams

INTRODUCTION

Homogeneous nucleation represents the generation of new phase embryos and their subsequent growth within the supersaturated initially homogeneous mother phase. Nucleation is a non-equilibrium thermodynamic phenomenon. A full understanding of nucleation is critical for accurate nucleation theory development, for new material design, for its role in atmosphere physical chemistry, etc [1-4]. Nucleation theory such as vapor/liquid, is currently insufficient to explain known phenomena. For example, it cannot deal with the existence of two-channel nucleation of vapor-to-liquid and vapor-to-solid near the triple point. Each nucleation channel is represented by an exponential nucleation rate surface of J over the P-T plane, where T is temperature and P is pressure [3, 4]. The multiplicity of the nucleation channels must be represented in the nucleation rate surface geometry, which is the sum of the individual phase exponential surfaces [3]. Measurement methods for the empirical study of vapor/liquid nucleation kinetics have been developing for more than a century. They have sufficient accuracy to detect the impact of phase transitions of the first or second order in a condensed phase on the vapor nucleation rate surface geometry [1-3].

Knowledge of the actual topologies of the nucleation rate surfaces is useful, for example, for development of the new material design technologies. It is currently not possible to have a common solution of the problem of creating nucleation rate surfaces. Thus, semi-empirical design of these surfaces can be extremely valuable [1-4]. The impact of phase transitions in a condensed phase on the geometry of the vapor nucleation rate surfaces is discussed in this study.

METHODOLOGY

A simplified case of nucleation kinetics can be presented for supersaturated single vapor nucleation. Nucleation can only occur when the mother phase is far enough from equilibrium, i.e. a vapor should be supersaturated. The chemical potential of the vapor phase, \( \mu_{vapor} \), exceeds the condensed phase, \( \mu_{cond} \), i.e. \( \mu_{vapor} - \mu_{cond} > 0 \). The nucleation rate, \( J \), can be expressed by the function: \( J = B \exp(-\Delta G^*/kT) \), where \( \mu_{cond} \) and \( \mu_{vapor} \) are the chemical potentials of the bulk phases; \( B \) is pre-exponential factor; \( \Delta G^* = n^*(\mu_{cond} - \mu_{vapor}) + f \) where \( n^* \) is number of molecules (or atoms) in the critical embryos of the new phase; \( f \) is the excess Gibbs energy of the critical cluster of the new phase containing \( n^* \) molecules as compared with the same number of molecules in a macroscopic sample of the mother phase, \( k \) is Boltzmann constant, and \( T \) is temperature.

The values of \( \mu_{cond} \) and \( f \) (equation 1) within the embryos have a discontinuity in the first derivative with respect to temperature at constant pressure in the mother phase. This discontinuity can be seen easily along the line of constant nucleation rate. That kind of nucleation rate surface singularity is detectable in the experimental data as described, for example, by Anisimov et al. [5].
It is known [4] that isotherms of single real gases have metastable areas in pressure-specific volume diagrams. These metastable areas are bounded by the bimodal and spinodal lines. The critical point, i.e. a phase transition of the second order, c, lies along the critical isotherm. A $P$-$T$ diagram generally has several lines of phase equilibria. Each equilibrium line can produce a surface for that phase transition. These surfaces can cross each other as can be seen on Fig. 1. The $P$-$T$ plane provides the base for a three-dimensional nucleation rate surface near the triple point. These nucleation surfaces cross each other along the line $et$, where the first derivative for constant $T$ or $P$ is discontinuous. That singularity shows the impact of the first order phase transition in the condensate on the nucleation rate surface. The curve, $v$, shows schematically the nucleation rate surface isotherm for the case of a phase transition of the second order. This kind of isotherm can be initiated by various second order phase transitions such as critical points (lines, etc), superconductivity, super fluidity, etc. [6-8]. In this case it is seen that vapor nucleation has two nucleation channels resulting in liquid droplets and solid particles [6].

The total nucleation rate, $J = J_l + J_s$, where the individual nucleation rates are measured for droplets, $J_l$, and solid particles, $J_s$. Each nucleation rate surface is represented by an exponential function. One should observe the resulting surface, $J(P, T)$, with a fold-like singularity. A phase transition can occur within the growing clusters. Linear relationships of the melting temperature with the reciprocal of the radius of small clusters were reported by Thompson [9]. However, several researchers have reported nonlinear relationships for these parameters [10, 11]. Computer modeling of the $T_m$ against $R^3$ relationship for Lennard-Jones clusters was performed by Samsonov et al. [12]. The computer experiments results were in agreement with experimental data and with independent thermodynamic considerations. We hypothesize that similar behavior can be found for nano-sized cluster melting or freezing when they have small values of the enthalpy of fusion. These singularities should generate additional singularity folds on the nucleation rate surfaces. Some phase transitions within small clusters cannot be observed because of the small quantity of the initial phase that is insufficient to permit new embryo formation.

**Fig. 1.** The nucleation rate surface at the triple point vicinity of a single system.

$J$ is rate of nucleation; $T$ is temperature, $P$ is pressure, $t$ is the triple point, line, $tc$, is vapor-liquid equilibria; line, $kt$, is vapor-solid equilibria. The equilibria lines continued to the conditions of metastable states (pieces $rt$ and $at$). Line, $cd$, presents the vapor sinodal. Dark grey surface shows the vapor to droplet transformation and light grey is presenting the vapor – solid transitions. Line, $Z$, illustrate schematically the isotherm for case of second order phase transition.
**CONCLUSIONS**

The phase transitions of the first and second order within a solid and liquid condensate have a clear impact on nucleation rate surface topologies for any system. These phase transitions produce singularities in the nucleation rate surfaces where there are discontinuities in the first or second derivatives. To detect these phase transitions, surface continuity and monotony can be used as suggested by Anisimov et al. [5]. A data base of phase equilibria diagrams and the nucleation rate surfaces that are related to these diagrams along with the algorithm for the design of these surfaces will provide a reliable basis for the understanding of a wide spectrum of technological, chemical, physical, material design, etc.
problems. Knowledge of the actual nucleation rate topologies can be extremely useful in the development of new technologies and optimization of existing ones to produce new materials with phase transitions, including technologies that involve catalysis, etc. This conceptual framework can be further extended to all energetic barrier systems.

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REFERENCES

MECHANISM OF FORMATION AND EXPLOSIBILITY OF THE ORGANIC NANOAEROSOL IN COAL MINES

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Keywords: coal mine, organic nanoaerosol, nucleation, frictional heating of coal, combustion of hydrocarbons.

INTRODUCTION

Explosions of methane- coal dust- air mixtures in mines represent serious risk. Most often, they result in catastrophic breakdown and mine worker deaths.

Investigation of the dust-air mixture ignition processes are carried out, starting from the end of the 19th century. As a rule, this process is studied in a spherical bomb, tube, or in a premixed flame with high dust level (1 – 100 g/m$^3$). During last decades the productivity of the mining machines has increased significantly. Their operation results in the formation of the nano-sized coal dust due to local heating of the rock, leading to evaporation of organic matter of the coal, with their follow-up condensation. Therefore, the investigation of the mechanisms of this nano-sized fraction of the coal aerosol and its influence on the combustion of the methane-dust-air mixture is of great importance.

METHODS

The coal samples for the laboratory studies were taken from the Kuzbass November 7th Mine (Leninsk-Kuznetsky, Russia).

For the laboratory study of nanoaerosol formation during the coal crushing, a grinding machine was constructed. The main unit of this set-up is a grinding mill. The grinding mill consists of the electric motor chamber and the grinding chamber 200 cm$^3$ in volume. In the latter chamber, coal is crushed by the rotating picks. The rotation frequency is 6000 revolutions per minute. An inert gas (Ar or He) comes to the inlet of the motor chamber and then to the grinding chamber with the flow rate of 3 - 10 cm$^3$/s. During coal crushing, the temperature in the grinding chamber is controlled by the K-type thermocouple. After the motor is switched on, the temperature quickly (in five minutes) reaches the stationary level of 80 °C.
To measure the nanoaerosol size spectrum and number concentration in both the coal mine and laboratory, the aerosol spectrometer (Dubtsov et al., 2017) and photoelectric counter were used. The size and shape of aerosol particles formed in the coal mine and in the laboratory grinding machine were studied using a JEM 100SX transmission electron microscope (TEM). Sampling for TEM is carried out thermophoretically.

Fig. 1 shows a typical size spectrum as obtained in the longwall. One can see the aerosol size spectrum revealed three modes, at about 10, 100 and 1000 nm. The TEM analyses showed that the first mode comes from the single (primary) particles formed by the homogeneous nucleation of supersaturated vapor, which was formed by the evaporation of the organic matter from coal due to the frictional heat release. The second mode particles are aggregates consisting of primary particles. These aggregates are formed by coagulation of primary particles. The third mode particles are formed by direct grinding of coal by the cutting picks. The number concentration of the coarse particles was measured to be in the range (0.5 - 2.0)×10^4 cm^-3, i.e. more than 90% of total number concentration comes from the nanosized particles.

Fig. 1. A typical size spectrum as measured at the longwall of coal mine.

Fig. 2. A typical size spectrum as measured at the outlet of grinding machine.

The size spectrum of aerosol particles as measured at the outlet of the grinding machine is shown in Fig. 2. One can see a good agreement between this spectrum and that measured in the coal mine (Fig. 1). Both spectra reveal the same modes at about 10 - 20, 100 - 200 and 1000 - 4000 nm, which are from single nanoparticles, aggregates and coarse particles formed by crushing, respectively. Therefore one can conclude that the grinding machine simulates the shearer well enough.

The chemical composition of organic nanoparticles formed by mechanical treatment of coal was studied in our previous paper (Valiulin et al,
The GC-MS analyses has shown that the chromatograms from coal extract were identical to these from organic nanoparticles except for light alkanes C_{10} - C_{13} which were absent in the chromatograms of particles (the vapour of these species was probably undersaturated in the nucleation zone). These results also support our assumption of the evaporation-nucleation mechanism of nanoparticle formation.

As the mass of organic aerosol formed at the longwall face can be large enough, the knowledge of the aerosol explosibility is of need. We extracted the coal-tar pitch by heating coal at a temperature of 620 K in the atmosphere of Ar for five hours. The coal-tar pitch sample, prepared in such a way, was then used to generate the organic aerosol without admixture of gaseous hydrocarbons (combustible gases). To this end, the pitch was placed into the flow heating chamber. The heating chamber consists of a horizontal quartz tube and an outer oven. The number concentration and mean diameter vs. the heating temperature are shown in Fig. 3 for the aerosol generated from the pitch by evaporation - nucleation.

The combustion of organic aerosol in the air (as well as methane/air mixtures) is studied in a spherical bomb with the volume of 10 L, built at the Institute of Chemical Kinetics and Combustion (Novosibirsk), equipped with the inlet and outlet ports with valves. The combustible mixture passes through the bomb during some time, then the inlet and outlet valves are closed. The centrally located Ni/Cr heater is used to ignite the mixture. The pressure is recorded with an inductive pressure transducer with the pressure range of 0 - 30 atm. Fig. 7 shows the pressure $P$ in the bomb after ignition as a function of time for the organic aerosol in the air (for two concentrations) and methane-air mixture. The curves demonstrate maxima corresponding to the time when the flame has reached the walls. The maximum times are about 0.4, 0.5 and 0.9 s for the aerosol of 100 g/m$^3$ (dense aerosol), methane-air of 42 g/m$^3$ and aerosol of 50 g/m$^3$ (lean aerosol), respectively, which means that the flame velocity is maximal for the dense aerosol and minimal for the lean one.

CONCLUSIONS

The formation of organic aerosol in the grinding machine has been studied. The size spectrum and morphology of aerosol from the grinding machine were close to those in the coal mine, which supported our assumption that the frictional heat release is the driving force for the formation of organic aerosol.

To demonstrate the explosibility of organic aerosol, we have generated them by heating coal-tar pitch to remove the effect from other explosive gaseous products of coal treatment. It was shown that even the organic aerosol mass with concentration of 50 g/m$^3$ is explosive. In view of the fact that the mass of organic aerosol formed from coal treatment is even higher than that of combustible
gaseous products, the formation of organic aerosol is to be taken into account when estimating the safety limits in coal mines.

Fig. 3. Aerosol number concentration and mean diameter at the outlet of the flow heating chamber charged by the coal-tar pitch as a feedstock vs. heating temperature.

Fig. 4. Pressure vs. time dependences for the combustion of aerosol in air and methane/air mixtures.

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REFERENCES


NON-EQUILIBRIUM CLUSTER PROPERTIES AND NON-ISOTHERMAL NUCLEATION

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Keywords: NUCLEATION, CONSTRAINT EQUILIBRIUM, LENNARD-JONES, CLUSTER.

INTRODUCTION

Almost all theories of the vapour to liquid nucleation are based on well-known kinetic approach. The kinetic part of the theories comprise the solution of death-birth equations with two boundary conditions giving two different steady state solutions, which can be related to each other. The balanced steady state solution is identified with equilibrium cluster distribution and this is crucial assumption sometimes called constraint equilibrium hypothesis (CEH). The validity of CEH was questioned many times (Lushnikov and Kulmala, 1998; Barrett, 2002; Ford and Harris, 2004; Bartell, 2009). The citation list is not full, and, perhaps, even the authors of the kinetic approach were in doubts equalising the balanced steady state to conditions for equilibrium. However it was the only way to advance in nucleation theory at that time. Nowadays the computer simulations can help in studying the validity of CEH. It has been reported about the brake of CEH (Zhuo, 2005) in MD simulations of argon nucleation. In our opinion it is not possible to deduce from those simulations about the brake of CEH. They rather demonstrate that evaporation and condensation rates are different in balanced and unbalanced steady states. That is not surprising since the conditions of the simulations were at the vapour densities close to the liquid ones, so the process can hardly be called vapour to liquid nucleation. In the present study we carefully examine the assumptions involved in the basis of the nucleation theories. Particularly we study the conditions of the kinetic scheme applicability and limits when CEH can be used. The Lennard-Jones vapour is used as an example.

RESULTS AND DISCUSSION

Suppose we have ensemble of $n$-clusters where their energy $E$ is distributed according to normalized function

$$\varphi(E) = \frac{1}{N_n} \frac{dN_n(E)}{dE},$$

(1)

where $N_n(E)$ is the number of $n$-clusters with energy less than $E$, $N_n$ is the total number of $n$-clusters. We section the distribution function in equal narrow energy interval $\Delta E$ and label them with $i$ index, so the number of cluster with energy $E_i$ equals to

$$\Delta N_{n,i} = N_n\varphi(E_i)\Delta E.$$ 

(2)

The clusters evolution with time $t$ is described by death-birth kinetic equations

$$\frac{\partial \Delta N_{n,i}}{\partial t} = \alpha_{n+1,\rightarrow i} N_{n+1} + \beta_{n-1,\rightarrow s} N_{n-1} - (\alpha_{n,i,\rightarrow} + \beta_{n,\rightarrow i}) \Delta N_{n,i}$$

$$- \sum_k (\gamma_{n,i,\rightarrow k} \Delta N_{n,i} - \gamma_{n,k,\rightarrow i} \Delta N_{n,k}),$$

(3)
where $\beta$ is the monomer condensation rate, $\alpha$ is the evaporation rate, $\gamma_{n,i \to k}$ is a rate of transition for the $n$-cluster from energy $E_i$ to $E_k$ induced by collision with carrier gas molecules, in the indexes of evaporation and condensation rates the sharp end of the arrow points out the final energy value of transition and the blunt end of the arrow shows the initial one. If one of them is not specified it means that the quantity is integral and evaporation/condensation occurs to or from all possible energy values. Knowing all the coefficients in Eq. (3) provides the possibility to calculate nucleation rate.

To obtain the condensation rates, the collision cross section (CCS) between the cluster and the monomer is geometrically estimated by a simple brute-force Monte Carlo method. We consider each atom of a cluster as a sphere with radius $r$, and the cluster is association of such spheres. The random trajectories of colliding monomers are produced by generating two random points on a sphere with a radius larger than $r_{\text{ref}}$ serving as a reference surface area measure. The line between these two points is the axis of a cylinder with radius $r$. The corresponding hits are counted if the cylinder has an intersection with the reference sphere or the cluster. The possible intersection can be calculated by basic vector calculus: if the distance from a cluster point to the line is less than $r$ the monomer hits the cluster. Several thousands of random trajectories are generated in order to get good statistics. The results are presented in Figure 1(b).

Figure 1: (a) Evaporation rate as a function of the total cluster energy per molecule. (b) Collision cross section as a function of cluster size obtained with the brute-force Monte Carlo method (solid line) for $r = 2.5$ Å. The dashed line corresponds the collision cross section of spherical cluster with bulk liquid density of argon at 50 K.

The evaporation rates are obtained through (MD) simulations. The examples of the results are presented in Figure 1(a). The transition rates $\gamma_{n,i \to k}$ are calculated assuming that the carrier gas atoms elastically collide with the cluster atoms. The calculations of CCS have free parameter $r$. To define it we consider the system at formally infinitely high concentrations of the carrier gas. According to general principle of Statistical Mechanics the carrier gas serving as a thermostat brings all the cluster to equilibrium in this case. Therefore the balanced steady state solution of Eqs. (3) must satisfy Boltzmann distribution. In other words, the detailed balance in the following form must hold

$$
N_n \int_{-\infty}^{\infty} \beta_n(E) \varphi_n(E) dE = N_{n+1} \int_{-\infty}^{\infty} \alpha_{n+1}(E) \varphi_{n+1}(E) dE,
$$

(4)
where \( \varphi_n(E) \) has the energy distribution corresponding to the Boltzmann one. As a matter of fact, to satisfy Eq. (4) radius \( r \) appears to have reasonable value for each cluster size. Provided it is done we have everything for solving Eqs. (3) at arbitrary conditions.

The massive data of evaporation rates in wide ranges of energies and cluster sizes obtained in this study for the solution of the kinetic equations has also self-worth. It can be used to analyze the validity of the existing theories for the cluster evaporation. To our knowledge this is a first systematic study of such kind. However, the main goal is to check the validity of CEH and compare the results to non-isothermal nucleation theory. The study is in progress and the results are to be presented at the Conference.

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REFERENCES


METASTABLE PHASE DECAY AT THE DECREASING RATE OF GROWTH

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INTRODUCTION

There exist enough situations in nature when the rate of the droplets growth decreases in time. Situation with the decreasing rate of growth takes place in the processes of cementation, structural transformations, morphological transitions, etc. The reaction of environment of a growing object leads to the decrease of the rate of growth of a new object.

The standard methods do not work in the situation of the decreasing rate of growth of the new phase embryos. This situation requires a special consideration which will be given below.

It is natural to consider two types of external conditions: The first type is a situation of decay. The second type of external conditions are the dynamic conditions when the smooth behavior of external influence in time takes place. Here we shall consider the situation of decay of the metastable phase.

We shall use the exponential powers for the law of the embryos growth. The application of exponential powers is explained by the absence of any dimensional parameter. The diffusion regime and the free molecular regime have also this form. Namely

$$\nu = t^\alpha \quad (1)$$

with a parameter $\alpha$. Exponential powers in the current consideration are smaller than that for the diffusion growth. The dependencies with $0 < \alpha < 1$ will be referred as the slow rates of growth. We shall namely this case. Dependencies with $1 < \alpha < 3/2$ are considered by the same methods as $0 < \alpha < 1$.

On the base of $\nu = t^\alpha$ it is very easy to introduce $z = \nu^{1/\alpha}$ to measure the time as the size of an embryo born in some characteristic moment (ordinary initial moment) of time.

We investigate the case of the homogeneous phase transition.

EVOLUTION EQUATIONS

Situation with the slow rate of growth is more complex than the avalanche consumption (the traditional situation) because here not only the droplets with relatively big sizes are the main consumers of vapor. Here all droplets take place in consumption of vapor. But now there is no necessity to consider the density profiles or profiles of the power of metastability.

The statement about the leading role of the supercritical embryos in the substance balance remains valid for $0 < \alpha < 3/2$. The case $\alpha = 0$ can be investigated explicitly (due to simple conservation laws) without this assumption. The case $\alpha = 0$ has a simple physical sense. When $\alpha = 0$ in the system there appeared embryos with a fixed size which do not grow.

The statement about the applicability of the quasistationary approximation for the rate of nucleation (the rate of appearance of droplets) can be also proven here analytically. Both mentioned
statements take place when $\alpha > 0$ in conditions of applicability of the macroscopic description of the critical embryo.

The power of metastability will be described by the value of the supersaturation

$$\zeta = (n - n_\infty)/n_\infty$$

where $n$ is the molecular number density of the mother phase, $n_\infty$ is the same value but for the phase equilibrium.

The evolution equation for the decay conditions can be written as

$$G(z) = A \int_0^z (z - x)^\alpha \exp(-G(x)) dx$$

with a positive parameter $A$. Here $G$ is the scaled number of molecules in a liquid phase, $z$ is the size of the droplet which was born at the very beginning of the nucleation process (the size means here the variable with the law of growth independent on the value of this variable).

The spectrum of the embryos sizes is

$$f \sim \exp(-G)$$

In the derivation we have used the following approximation for the stationary rate of nucleation

$$f_n(\zeta) = f_n(\zeta_0) \exp(\Gamma(\zeta - \zeta_0))$$

as a function of the supersaturation $\zeta$ where index 0 characterizes the base of decomposition. Here $-\Gamma$ is the derivative of the free energy of a critical embryo formation over $\zeta$. One can show that $\Gamma$ has the scale of the number of molecules in critical embryo. Instead of the classical theory of nucleation one can use here any other approach which ensures (5) with $\Gamma \gg 1$.

We need the validity of this approximation only at some relatively short range of supersaturation where $\exp(\Gamma(\zeta - \zeta_0))$ changes only $e$ times.

UNIVERSAL SOLUTION

Equation (3) after the evident scaling $z \to A^{1/(\alpha+1)} z, x \to A^{1/(\alpha+1)} x$ leads to

$$G = \int_0^z (z - x)^\alpha \exp(-G) dx$$

without parameters. Then $G$ is the universal function and the zero momentum $M_0 = \int_0^\infty \exp(-G(x)) dx$ is the universal constant. Since $M_0$ is the coefficient in the asymptotically leading term $M_0 z^\alpha$ in the expression for $G$ after the end of nucleation then the universal constant $M_0$ accumulates all information necessary for further evolution.

One can determine the duration of nucleation period $\delta z$ by relation

$$N(\delta z) = N(\infty)(1 - \epsilon)$$

with some small parameter $\epsilon$ (here $N(z)$ is the number of droplets appeared before $z$). Since $z$ is equivalent to the time it is possible to speak about the number of droplets appeared before $z$. More rigorously $N(z)$ is the number of droplets appeared before the moment of time when the size of the droplet appeared at the initial moment of time will attain the value of $z$.

\footnote{Except $\alpha$.}
Since the rate of nucleation decreases rather rapidly one can get for the reasonably small $\epsilon \approx 0.05 \div 0.1$ the characteristic value of $\delta z$ which corresponds to the duration of the nucleation period. Since the rate of growth is known one can recalculate the value $\delta z$ in the time of duration of the period of intensive nucleation. The value of the droplets number

$$N(z) \sim \int_{\delta z}^{z} \exp(-G) dx$$  \hspace{1cm} (8)$$

is also the universal function and $\delta z$ as the root of equation with no parameters will be the universal constant.

Now we shall construct the form of the spectrum of embryos sizes explicitly.

To propose another iteration procedure we shall get an important property typical for the regime of the slow growth.

**THE PROPERTY OF THE EFFECTIVE SIZE OF GROWTH**

For every moment $z$ (or $t(z)$) we can find the boundary $z_0$ with two properties

- $z_0 \ll z$
- $\nu(z) - \nu(z_0) \ll \nu(z)$

One can see that for $z_0 = \alpha z/p$, $p \sim 2 \div 3$ both properties are satisfied.

It means that the qualitative picture is the following: rather soon a droplet accumulates the main quantity of vapor and later the further accumulation is not too important. Certainly, the moment $z_0$ of effective accumulation grows in time. There is no unique recipe to choose $z_0$, one can speak about the characteristic interval of possible values of $z_0$. Any choice from this interval is possible.

This picture allows to suggest the following initial approximation:

*For every $z$ one can imagine that practically immediately after creation of a droplet the number of molecules of a given droplet (with coordinate $z$) attains the value $\nu(z_0)$ and then the droplet does not grow rapidly.*

One has to stress that for different $z$ the values $z_0$ are also different. But for some rather short time interval like the interval of time corresponding to the formation of the back side of the head of the spectrum of the droplets sizes one can speak about the characteristic constant $z_0$.

The mentioned property allows to use the approximation with $\alpha = 0$ as the initial approximation. The solution in this case has a simple explicit form. One has to note that this property is no more than an approximation. But it is used here only as the initial step in the iteration procedure. Further steps will give better results.

The case $\alpha = 0$ can be solved analytically, because it can be reduced to the ordinary differential equation of the first order. This leads to $\exp(-G) = 1/1 + z$. The last equation gives the infinite number of droplets appeared in the process of nucleation. We come to an error initiated by the use of approximation (5) at the small supersaturations. Really, at $G = n - n_\infty$ the rate of nucleation has to be zero, but approximation (5) gives the finite value of the nucleation rate at any $G$.

We are not interested in the long tail $\sim z^{-1}$ of the spectrum of the embryo sizes because this tail can not be directly seen in experiment. Integral values in this situation can be explicitly calculated without knowledge of the tail. Really, the total number of droplets can be easily obtained, it is convenient to get it even in initial variables by the following procedure:
The case $\alpha = 0$ corresponds to a fixed number $\nu_{\text{fin}}$ of a number of molecules inside the droplet. This quantity does not depend on time (in the scaled units $\nu_{\text{fin}} = 1$). In this case some evolution occurs since here we introduce the quantity $\nu_{\text{fin}}$ of the number of molecules.

The total number of droplets can be calculated very easy

$$N_{\text{total}} = \frac{n - n_{\infty}}{\nu_{\text{fin}}} \quad (9)$$

We can choose the cut-off of the spectrum of the embryos sizes at the size where $N(z) \sim \text{const} + \int^z (1 + z)^{-1} dz$ equals to $N_{\text{total}}$.

**ITERATION PROCEDURE**

One can see that even in the case of small positive $\alpha$ the spectrum of the embryos sizes is concentrated in the fixed region. This allows to use the iteration procedure

$$G_{i+1} = \int_0^z (z - x)^{\alpha} \exp(-G_i) dx \quad (10)$$

Here the lower index denotes the number of iteration. As the initial approximation we choose the analytical solution for $\alpha = 0$, i.e.

$$G_0 = - \ln(x + 1) \quad (11)$$

This differs from consideration of the situations with the avalanche regimes of growth, where $G_0 = 0$. One can easily prove that it converges to the real solution.

The first iteration can be easily calculated. We have

$$G_1 = - \frac{z^{\alpha+1}}{z + 1} \Phi\left(-\frac{z}{z + 1}, 1, \alpha + 1\right) \quad (12)$$

where $\Phi(z, s, v) = \sum_{k=0}^\infty \frac{z^k}{(s + k)^v}$ is the standard special function.

The spectrum of the embryos sizes $\exp(-G_1)$ can be considered as a good approximation. This property can be shown both analytically and numerically. The relative error in the number of droplets, i.e. in

$$N(z) = \int_0^z \exp(-G(x)) dx \quad (13)$$

is less than 0.05 for $\alpha < 0.5$. The last integration can be fulfilled by means of the steepest descent method with a maximum at the boundary point.

The values $\alpha$ from $1/2$ up to $3/2$ can be considered analogously but on the base of iterations started from solution with $\alpha = 1$. This solution can be found analytically, since the evolution equation can be reduced to the automorphic second order ordinary differential equation. Then it is necessary to take one iteration step and then to integrate $\exp(-G_1)$ over time to get the number of droplets. The last integration can be fulfilled by means of the steepest descent method. Here one can make the explicit extraction of the rectangular zone for $\alpha > 1$. The relative error is rather small. This fact can be shown both numerically and analytically.

Details of this approach can be found in [Kurasov, 2015].

**REFERENCES**


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2 More accurate is to write $N_{\text{total}} \nu_{\text{fin}} = n - n_{\infty} + 2a/3\nu_{\text{fin}}^{1/3}$ where $a$ is renormalized surface tension
INTRODUCTION

The detailed nucleation mechanism controlling particle formation in vehicle exhaust is currently unknown. The concentration of sulfuric acid vapor has been found to correlate with the particle number concentration in vehicle exhaust (Arnold et al., 2012; Rönkkö et al., 2013). Therefore, binary sulfuric acid-water nucleation can be considered an acceptable candidate for the nucleation mechanism.

Due to the nature of vehicle exhaust plumes, the concentrations of sulfuric acid ([H$_2$SO$_4$]) and water ([H$_2$O]) vapors and temperature (T) do not remain constants while hot raw exhaust is diluting and cooling after being emitted from the tail pipe. Modeling studies simulating particle formation in vehicle exhaust require a nucleation rate function that is explicitly defined in these varying conditions, say

$$J = J([\text{H}_2\text{SO}_4],[\text{H}_2\text{O}],T).$$

(1)

The classical nucleation theory provides a function of this kind, but there are large discrepancies between the theoretical and experimental nucleation rates in the case of binary H$_2$SO$_4$-H$_2$O nucleation (Olin et al., 2015). Many nucleation experiments report nucleation rates in the following form:

$$J = k[\text{H}_2\text{SO}_4]^n$$

(2)

where $k$ and $n$ are an empirically defined constant and a slope parameter, respectively. Because the constant $n$ ignores all effects of temperature and the water concentration, and the sulfuric acid concentrations in the experiments were usually within an atmospherically relevant range, i.e. at a lower level compared to the concentrations in vehicle exhaust plumes, Eq. (2) cannot be used to simulate particle formation in vehicle exhaust.

Particle formation and growth in vehicle exhaust has been studied using a sampling system consisting of a porous tube type diluter, an aging chamber and an ejector diluter (Ntziachristos et al., 2004; Arnold et al., 2012; Rönkkö et al., 2013; Karjalainen et al., 2014). The sampling system is found to mimic particle formation and growth processes occurring in a real-world driving case relatively well (Rönkkö et al., 2006). In our study we use the sampling system to examine the nucleation rates occurring in vehicle exhaust.

The simplest way to obtain nucleation rates from the measurement data is to divide the particle number concentrations with an assumed, and usually a constant, nucleation time. Additionally, the effects of, e.g., coagulation and gaseous and particulate losses must be taken into account in solving the nucleation rates using the measured concentration data. In the case of a measurement involving flowing fluid, a constant nucleation time denotes a constant nucleation region. However, in a diluting and cooling sampling system, the region cannot be considered constant because it
is affected by both the slope parameter and the rates of dilution and cooling. Therefore, it is important to model aerosol dynamics in the whole spatial domain of the sampling system. In that way, also the other processes, such as coagulation and losses, will be simulated explicitly. Because the sampling system contains some turbulent regions causing backward flows, we use computational fluid dynamics (CFD) modelling to solve the flow field in two-dimensional space and apply the aerosol dynamics model into it. In other words, we model the nucleation rate in every computational cell in the spatial domain with Eq. (1) where the concentrations and temperature have the local values, not, e.g., the initial or the average values.

METHODS

To examine the nucleation rates of $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ nucleation, real vehicle exhaust was not used as the sample due to its complex composition. Instead, sulfuric acid and water vapors were used. Both vapors were generated by bubbling pure liquid that had a specified temperature. After mixing of the vapors the gas mixture was heated to exhaust-relevant temperatures. The resulting gas mixture is considered the raw exhaust sample, but which consists of sulfuric acid and water only. The concentrations of the vapors in the raw sample depend on the liquid temperature through the saturation vapor pressure curves. This dependence was validated by measurements with CI-API-TOF from the gaseous sample and with ion chromatography from the liquid sample made by bubbling the gas to water. The raw sample was diluted and cooled using the sampling system described before and measured using Airmodus Particle Size Magnifier (PSM), TSI Ultrafine Condensation Particle Counter 3775 (CPC), and TSI Nano Scanning Mobility Particle Sizer (SMPS).

The aerosol dynamics model CFD-TUTEAM (Tampere University of Technology Aerosol Model for Computational Fluid Dynamics) coupled with the commercial Ansys Fluent 17.1 CFD software is used to model the nucleation rates inversely. In other words, different values for the parameters in Eq. (1) are inputs for the model, and the size distributions output by the model are compared with the measured size distributions.

RESULTS AND CONCLUSIONS

The experimental data covers a sulphuric acid concentration range from $10^{12} - 10^{14}$ cm$^{-3}$ (Figure 1), considerably higher than in traditional atmospheric studies (Sipilä et al., 2010; Dal Maso et al., 2016). Correspondingly, also particle number concentrations were very high, in the range of $10^6 - 10^9$ cm$^{-3}$. The power law dependence of number and gas phase concentration showed the slope $n$ of 1 – 2. Previous studies with similar dilution systems have shown that the slope for number concentration corresponds fairly well to nucleation rate slopes (Olin et al., 2015).

The results of our measurements represent to our knowledge the first dataset of sulphuric acid nucleation studies at exhaust-relevant conditions using sub-3 nm particle detection instrumentation. Thus, it will provide new insights on the formation of ultrafine particles from vehicle exhaust, and the influence of, e.g., oxidating catalysts to such emissions.

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Figure 1: Particle number concentration as a function of the sulfuric acid concentration in the raw sample.

REFERENCES


PROBING STRUCTURE AND CHEMICAL PROPERTIES OF FREESTANDING CLUSTERS WITH SYNCHROTRON RADIATION. PART I: THE MUSCLE CLUSTER SOURCE.

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Keywords: Synchrotron radiation, photoelectron spectroscopy, free nanoclusters.

INTRODUCTION

Despite intensive laboratory and field measurements, dating back to pioneering works of Tyndall, R. von Helmoltz, Wilson, Aitken, and others over a century ago, molecular details of formation and growth of new atmospheric particles remain elusive. As changes in new particle formation and growth rates can affect the global concentration of cloud condensation nuclei and thus contribute to anthropogenic radiative forcing (Merikanto et al., 2009), a mechanistic understanding of these processes, including phase and surface properties of newly formed particles, is vital for reducing uncertainties in climate forecasts. Deductions based on indirect measurements have proven inconclusive (Kupiainen-Määtä et al., 2014), and recently there has been a surge towards measurements setups yielding molecular-level resolution of cluster properties. Surfaces in particular are currently receiving increasing attention from the atmospheric science community. A suite of novel developments in methods originating from materials science now allow for highly surface sensitive chemical characterization of systems with increasing resemblance to atmospheric aerosols.

Here, we present a custom-built experimental setup (Hautala et al., in preparation) to produce and directly characterize chemical, structural, and phase-state properties of freestanding neutral multicomponent nanoclusters with well-defined composition, using synchrotron radiation based spectroscopy at the gas-phase endstation of the FinEstBeaMS beamline, MAX IV Laboratory. The unsurpassed brightness of the new MAX IV synchrotron light source has made feasible the use of powerful surface sensitive photoelectron spectroscopy techniques for samples of relatively low density, and in particular freestanding cluster beams of atmospherically relevant trace components.

METHODS

Synchrotron radiation (SR) is bright light produced by electrons orbiting at a velocity close to the speed of light in a dedicated accelerator, or storage ring. SR is an extremely powerful research tool, but its generation requires a large and dedicated facility which is well beyond the financial means of most academic institutions and companies. The MAX IV Laboratory (www.maxlab.lu.se) is a new generation SR light source built in Lund, Sweden. The magnetic structure of the storage ring is based on the Multibend Achromat innovation, providing unique properties and superior brightness of the light, compared to older generations of SR facilities (Tavares et al., 2014). The Finnish Estonian Beamline for Materials Sciences (FinEstBeaMS) is located at the 1.5 GeV storage ring of the new MAX IV facility. The beamline is dedicated to providing world-class radiation with precisely controlled and widely variable parameters, with applications ranging from electronic structure studies of atoms and molecules to nanoscale investigation of multiphase systems and their
interfaces. FinEstBeaMS provides undulator radiation with flexibly controlled polarization in the energy range of 4.3–1000 eV, where the maximum flux (∼5×10^{13} photons/s) is provided around 150 eV. The beamline hosts a gas-phase experimental end station capable of PES (high resolution hemispherical analyzer), ion mass spectroscopy (Time-of-Flight with imaging possibilities) and absorption spectroscopy, with further possibilities for luminescence studies and the so called solid state branch enables surface studies of in-situ and ex-situ deposited samples. Of particular interest to atmospherically relevant studies, the versatile setup of the gas-phase end station offers a range of possibilities to flexibly connect additional user experiments.

The custom-built Multiuse Setup for Clusters Emission (MUSCLE) for producing and introducing freestanding nanoparticles to the synchrotron beam is shown in Figure 1. MUSCLE is our next generation cluster source based on the proven basic design of the Exchange Metal Cluster (EXMEC) source (Huttula et al., 2010). Both setups generate a continuously renewed beam of neutral clusters comprising a wide range of atomic, molecular or ionic components. MUSCLE and EXMEC share the same principles of operation, which can be divided into two stages: 1. adiabatic expansion, and 2. pick-up. In the first stage, clusters are generated by letting a gas-phase substance or mixture pass through a converging–diverging nozzle into vacuum. Substances, such as water, which are liquids under ambient conditions, are vapourized prior the nozzle by simple thermal heating. These precursor substances are handled to ensure that no ionization or other charging takes place and neutrality is preserved. A remarkably broad range of clusters can be generated using only this first stage of the cluster source. The generated cluster size distribution and properties (e.g. internal temperature) are controlled by variables such as gas pressure just before the nozzle, nozzle temperature and dimensions (orifice size and geometry), and the gas composition. Clusters have been generated, either by us or by other research groups, from rare gases, molecular gases (e.g. oxygen, hydrocarbons), or substances which are liquid at ambient conditions (e.g. water, different alcohols), as well as combinations of these.

The second (pick-up) stage of the cluster source can in principle be used in two different ways. First, as a mechanism for doping the (host) clusters formed in the first stage with a controlled amount of some other substance. This produces a mixed cluster and has been used to generate for example alkali halide containing water clusters (Partanen et al., 2013). Second, if doping is taken to extreme, the initial host cluster can be completely converted to a cluster made up purely of the dopant substance. The latter case is referred to as the exchange method and has been used successfully to create neutral clusters from very low-volatility elements, such as metals (?), inorganic compounds, such as alkali halide salts (Hautala et al., 2014), but also from semivolatile atmospheric organics like stearic acid (unpublished data). In both cases, the substance to be doped or exchanged is introduced to the first-stage host clusters by thermal evaporation of a solid to create a gas phase vapor. Host clusters are passed through the vapor, picking up dopant atoms/molecules on the fly. The amount of substance picked up depends on variables related to both host cluster (size, pick-up cross section) and dopant material (vapor pressure), as well as the apparatus dimensions (length and residence time in the pick-up region).

In the newest MUSCLE setup, several updates have been made. Main extensions include the addition of one extra liquid precursor and pick-up oven. This allows the use of two different precursors in the first stage with controllable mixing ratio, or doping two different solid substances to the same host cluster with independent control over the amount of each substance doped. A further addition is the inclusion of a gas phase collision cell for cases where the dopant is easily introduced into gas phase (volatile or semivolatile). These type of collision cells have also been used for performing chemical reactivity studies on clusters. In it’s current configuration, the MUSCLE setup thus comprises two thermally isolated evaporation ovens. This allows us to compose clusters of substances, which need not be directly miscible in the liquid phase, or from liquids with very different vapor pressures, which thus evaporate at very different temperatures or different ratios at
Figure 1: The main operational parts of next generation cluster source MUSCLE (Multiuse Setup for Clusters Emission): adiabatic expansion stage, pick-up/exchange stage, cluster beam, and interaction region with synchrotron radiation.

a given temperature. As some of the components of MUSCLE were completed only in 2016, many of its new capabilities are still unexplored.

Photoelectron spectroscopy (PES) is based on ionizing a sample with photons of known energy and subsequently detecting the emitted (photo)electrons. The fundamental observables are the kinetic energy and angular distribution of the photoelectrons, from which all additional information is constructed. Two factors make PES highly suitable for studying clusters and multicomponent nanoparticles. First, PES is highly surface sensitive and thus well-suited for nanoscale systems. Second, PES provides high chemical selectivity, where the measured signal is dependent on both the target element and its chemical environment, including the identity, number, and charge state of neighboring atoms, bond lengths, etc. These variables are all reflected in the electronic structure of atoms, allowing a suite of information to be extracted PES. For example, it is often possible to separate the signals from atoms, molecules, or ions in the respective surface and bulk regions of the cluster. We have used this to study how alkali metal and halide ions are non-uniformly distributed with respect to one another, and between the surface and bulk of water clusters (Hautala et al., in preparation). In some cases, even atoms residing in different coordination sites on the cluster surface can be distinguished, as we have recently demonstrated for small alkali halide clusters (Hautala et al., 2014; Hautala et al., 2016).

CONCLUSIONS

There are, of course, multiple ways to produce nanoscale clusters, some of which have been used to characterize mixed clusters (Pathak et al., 2014; Tao et al., 2016). In addition, mixed cluster properties and composition have been studied extensively using indirect methods (e.g. nucleation theorems) that require condensation growth and optical detection. The novelty of our approach lies in the combination of PES and other SR spectroscopic techniques that provide direct, genuine molecular level information, with cluster production using our new cluster source MUSCLE, which is capable of changing cluster properties (e.g. size and composition) in a systematic and controlled manner. This allows for additional degrees of freedom in experiments, to study how specific changes affect the overall cluster properties. To our knowledge, there are currently no or few setups (Wyslouzik and Wölk, 2016) capable of providing detailed information of the phase and mixing state of clusters in the full size range we are exploring here, without relying on indirect estimations based
e.g. on nucleation theorems.

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REFERENCES


WATER ACCOMMODATION ON ICE

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Keywords: water accommodation, accommodation coefficient, water condensation, vapour deposition on ice, molecular dynamics, premelting layer, disordered interface of ice.

INTRODUCTION

Condensation of water molecules from the vapour phase onto liquid water and ice surfaces plays a crucial role in atmospheric processes such as cloud formation. In the present study we focus on the accommodation of water from the surface into the bulk crystalline ice phase. The accommodation is affected by the disordered interface (Bartels-Rausch et al., 2014) (here also referred to as “premelting layer”) at the ice-vapour interface and the bulk accommodation generally requires knowledge of the processes occurring at (a) the vapour–premelting layer and (b) the premelting layer–ice interfaces. Experimental data suggest that the bulk accommodation coefficient decreases with increasing temperature but the data from different experiments are spread over a large range of values indicating a large uncertainty (Kong et al., 2014; Skrotzki et al., 2013). The approach presented here combines a refined analysis of recent experimental data with results obtained from molecular dynamics (MD) simulations with the goal to narrow down uncertainties in the water accommodation coefficient on ice.

METHODS

In the present study we re-analyse recent experimental data for the accommodation coefficient of water on ice (Kong et al., 2014) obtained with an environmental molecular beam method within the framework of a binary mixture. The experiment is based on the measurement of the absorbed fraction of the beam from an ice surface subjected to a pulsed molecular beam of D₂O and, using information about the pulse intensity, conclusions about the accommodated fraction can be drawn. Assuming an interfacial mole fraction of D₂O, Xₐ, we calculate the time dependent intensity

\[ I(t) = Xₐ k_{\text{D}_2\text{O}} k_{\text{D}_2\text{O}} \exp \left[ -(k_{\text{evap}} + k_{\text{acc}}) t \right], \]  \hspace{1cm} (1)

where \( k_{\text{evap}} \) and \( k_{\text{acc}} \) denote the evaporation and accommodation rate for D₂O from the premelting layer to the gas phase and into ice, respectively. Eq. (1) can be used to fit the experimental time-of-flight (TOF) data. Integration over the experimental time interval \( \tau \) then gives

\[ \int_{t_0}^{t_1} I(t) \, dt \]
the desorbed fraction and thus the bulk accommodation coefficient becomes
\[
\alpha_b = 1 - X_s \frac{k_{D_2O}^{\text{evap}}}{k_{D_2O}^{\text{evap}} + k_{D_2O}^{\text{acc}}} \left\{ 1 - \exp \left[ -\left( \frac{k_{D_2O}^{\text{evap}} + k_{D_2O}^{\text{acc}}}{k_{D_2O}^{\text{evap}}} \right) \right] \right\}.
\]
In the present approach we intend to utilise additional information to constrain the data:

1. We use MD simulations and apply the Umbrella sampling technique to determine the free energy for a single vapour molecule approaching or leaving an ice surface (fig. 1). The simulations indicate a barrier-free uptake or evaporation into and from the premelting layer, consistent with analogous simulations of the liquid water surface (Varilly and Chandler, 2014). The vapour–premelting layer accommodation coefficient is consequently set to unity, as also suggested by other studies of the liquid-vapour interface (Julin et al., 2013), which effectively constrains \( k_{D_2O}^{\text{evap}} \).

2. As mentioned above, the surface of ice is known to be disordered with the water molecules at the interface being more mobile than in the bulk crystal (Bartels-Rausch et al., 2014). The thickness of this premelting layer depends on temperature (Bluhm et al., 2002; Dash et al., 2006; Conde et al., 2008). We combine the analysis with MD simulations to gain a molecular level insight into the role of the disordered interfacial layer for the accommodation process. Information about the pulse intensity, its duration and the thickness of the premelting layer can, e.g., be used to determine the interfacial mole fraction \( X_s \).

With results from experiments, MD simulations and theory we thus aim to narrow the uncertainties and obtain a refined estimate for the water accommodation coefficient on ice.

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REFERENCES


FORMATION EVENTS OF INTERMEDIATE AIR IONS AT TAHKUSE OBSERVATORY IN
1995–2016

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Keywords: AIR IONS, NUCLEATION EVENTS.

INTRODUCTION

Air ions are known as carriers of electric current and space charge in the atmosphere, but they are also
involved in the new-particle formation (NPF). The importance of new-particle formation and air ionization
on the Earth’s climate has been discussed in many papers (e.g., Tinsley and Yu, 2004; Carslaw et al.,
2010). The nucleation events were frequently observed at many places in Europe (Manninen et al., 2010;
Nieminen et al., 2014; Birmili et al., 2016) and in the world (Hirsikko et al., 2011). However, the particle
formation mechanisms are still not fairly known despite of recent developments in the application of high-
 tech (mass spectrometric) measuring techniques to identify the chemical precursors involved in the NPF
process (Luts et al., 2011; Kourtchev et al., 2013; Bianchi et al., 2016; Kirkby et al., 2016). The robust
methods of particle and air ion mobility spectrometry can still provide valuable information to study the
NPF events on statistical bases, starting from the size range of smallest stable structures - cluster ions
(Hörrak et al., 2008). Intermediate air ions represent the charged fraction of the smallest stable aerosol
particles in the diameter interval of 1.6–7.4 nm and can be used to study the NPF in the atmosphere
(Hörrak et al., 2000).

In this abstract we present the preliminary results of the NPF event classification, annual frequency and
growth rate of nanometer particles (intermediate air ions) on the bases of long term measurements of size

METHODS

Tahkuse Observatory (58°31’N 24°56’E) is located in a sparsely populated rural region in the south-
western part of Estonia, at eastern shore of Pärnu river. The nearest city Pärnu with 40000 inhabitants is
located about 25 km to south-west and Soomaa National Park (bogs and wetlands preserve) about 8 km
south-east from the station.

Air ion size distributions are measured by Air Ion Spectrometer (AIS), which covers the size range of 0.8–
79 nm and Neutral cluster and Air Ion Spectrometer (NAIS), which covers the size range of 0.8–42 nm,
according to Millikan formula (Hörrak et al., 2000; Mirme et al., 2007). Long term measurements took
place from March 1995 to December 2016. The measurement data are available for 6765 days, which is
84.7 % of total days (Figure 1). The NAIS measurements started from July 2011.

Figure 1. Available data for the years 1995–2016. Green areas indicate available data, white areas missing
data and black areas days when class Ia nucleation events occurred.
We have classified the intermediate air ion formation events according to similar principles as described by Hirskikko et al. (2007), but taking into account the specificity of NPF events at Takhuse. Four classes of intermediate air ion formation events are probably associated with photochemical nucleation mechanism in fair weather conditions, that we call as “events” and one class with intermediate ion generation during precipitation, usually rain, we call those as “precipitation events”. In the case of nucleation “events”, a growth of newly formed particles can be seen. According to the shape of particle growth followed by the evolution of particle size distribution, these events can be classified as follows:

**Class Ia.** The formation and subsequent growth of particles is well developed. The size distribution has no deep gap between the cluster (below 1.6 nm) and intermediate ions indicating that the cluster ions are involved in the nucleation. The growth rate of particles can be calculated over entire measured size range.

**Class Ib.1.** Similarly to class Ia, the formation of particles starts from the cluster ion mode, but the growth of particles is suppressed before they reach to the sizes of 5–10 nm. The reason for this type of event might be an insufficient concentration of nucleating vapors.

**Class Ib.2.** The particle formation does not start from the cluster ion mode and low concentration gap exists between cluster and intermediate ions at about 2–3 nm.

**Featureless.** During these events the elevated concentration of intermediate ions is detected, which might be generated due to nucleation processes, but the shape of size distribution evolution is unclear and/or the duration of NPF is short (less than 1 hour) and we do not see growth of the particles.

**Precipitation (rain or snow).** During the events, the elevated concentration of negative intermediate ions with peak about 2–3 nm is detected. The balloelectric mechanism is considered to be the main reason of intermediate ion formation (Tammet, 2009; Lüts et al., 2009). The concentration of positive intermediate ions also increases, but usually it is 50% or less compared to negative ions, exception may occur in winter during snowfall or snowdrift.

**Undefined.** The reason of elevated concentration of intermediate ions is not known or it might be instrumental or local pollution effect.

**Non-event.** The concentration of intermediate ions in the size range of 1.6–7 nm remains below low background (50–100 cm⁻³) during whole day. The situation is similar to the stationary size distributions during night and early morning (about 0:00–6:00) shown in Figure 2, well before the nucleation onset. The examples of days associated with different event classes are depicted in the Figure 2 below.

![Figure 2. Examples of the NPF events and precipitation (rain) event (recorded in the afternoon 20120416). Color code indicates particle number concentration (cm⁻³).](image-url)
RESULTS

During the 21-year-long study period from 1995 to 2016, we found that the intermediate ion formation events had a clear seasonal variation with the maximum frequency during spring and the second maximum during autumn (Figure 3). Days with nucleation events (class Ia, Ib.1, Ib.2 or II) form about 14.1 % and days with one or more precipitation events 15.3 % of total measurement days, whereas 34.5 % of days are non-event days with no intermediate ion formation. Class Ia form 16.5 %, class Ib.1 24.4 %, class Ib.2 9.5 % and class II 50.1 % of total nucleation events. The growth rates of particles were calculated using maximum-concentration method (Hirsikko et al., 2005). Average (median) growth rates calculated from class Ia events for three size ranges (1.6–3 nm, 3–7 nm and 7–25 nm) were 2.5 (1.9), 5.0 (3.5) and 7.6 (5.3) nm h⁻¹ for negative and 3.5 (3.0), 7.0 (4.4) and 9.4 (6.1) nm h⁻¹ for positive ions respectively. The annual variation of negative ion growth rates are depicted in the Figure 4.

Figure 3. Annual variation of nucleation events (class Ia, Ib.1, Ib.2 and II), precipitation events and non-events. The numbers in the upper part of the figure indicate available data in percent for given month.

Figure 4. Annual variation of negative air ion growth rates in three size ranges: 1.6–3 nm (blue boxes), 3–7 nm (green boxes) and 7–25 nm (red boxes). Boxes indicate quartile ranges with median value at center. The numbers in the upper part of the figure indicate total number of events (class Ia) for given month.
ACKNOWLEDGEMENTS

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REFERENCES


Kinetic analysis of homogeneous droplet nucleation using large scale molecular dynamics simulation

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Keywords: Molecular Dynamics, Nucleation, Condensation.

INTRODUCTION

Both theoretical and experimental approaches to the study of homogeneous nucleation are well established. The classical nucleation theory (CNT) has been widely applied to understand nucleation, but estimates of the nucleation rate at which the critical nuclei are generated from CNT show significant differences from those obtained experiment (Wedekind, 2007). This is because of assumptions in the theory that treats a microscopic cluster as though it were a macroscopic droplet. In experiments, there are technical difficulties associated with analyzing the dynamics of nano-sized clusters. In order to investigate the dynamical process of nucleation at the molecular level, molecular dynamics (MD) simulation is effective.

Many studies of homogeneous droplet nucleation using MD have been performed since the study of Yasuoka and Matsumoto (Yasuoka and Matsumoto, 1998). However, the range of nucleation rates calculated from MD is orderly greater than those measured from experiments. One of the reasons for this discrepancy is due to the difference in the supersaturation ratio examined. Ideally, one would perform MD simulations with the same conditions as those used in comparative experimental studies, typically at supersaturation ratios below 10. However, computational restrictions make it difficult to observe nucleation at supersaturation ratio conditions that require long calculation times, which is coupled with a small number of molecules. Recently Diemand et al. presented a solution to this problem (Diemand, 2013). They performed MD simulations of systems large enough to observe nucleation at low supersaturation ratios and obtained a nucleation rate, which was almost in the same range of those of experiments. However, kinetic analysis on such large systems was lacking. Kinetic analysis allows us to identify clusters, and enables the estimation of critical nucleus size and cluster formation free energy directly from the simulation results. In addition, the critical cluster size can be large enough to adequately apply the capillarity approximation at low supersaturation ratio conditions. This will allow us to compare the simulation results with CNT and experiments more easily.

In this study, our research objectives are to carry out large-scale MD simulations of homogeneous droplet nucleation and to acquire the nucleation rate, critical nuclei size, and cluster formation free energy using kinetic analysis. Furthermore, the results from MD will be compared with those from CNT to test the validity of the methodology.

METHODS

At first, we will give a brief introduction on CNT. The nucleation rate in CNT, $J$ is written as

$$J = Z \beta(n^*) \rho_{eq}(n^*),$$  (1)

where $Z$, $\beta(n)$, and $\rho_{eq}(n)$ are the Zeldovich factor, forward rate, and the number density of supersaturated vapor at equilibrium state, respectively; moreover, $n^*$ is the critical nucleus size.
By converting the equilibrium state vapor density \( \rho_{eq} \) in Eq.(1) to that for a steady state \( \rho_{st} \), the steady state nucleation rate becomes

\[
J_{st} = \rho_l^{-1} \sqrt{\frac{2\gamma}{\pi m}} \rho_{st}^2 \exp \left( -\frac{\Delta G^*}{k_B T} \right), \tag{2}
\]

where \( \rho_l \) and \( \gamma \) are the number density of liquid state and the surface tension, respectively. The cluster formation free energy \( \Delta G^* \) is given as

\[
\Delta G^* = \frac{16\pi}{3} \frac{\gamma^3}{(k_B T \rho_l \ln S)^2}, \tag{3}
\]

where \( S \) is the supersaturation ratio.

In this study, the supersaturation ratio was defined as \( S = \rho_{at}/\rho_s(T) \), where \( \rho_s(T) \) is the number density of the saturated vapor at temperature \( T \). Using the number density of monomers \( \rho(1) \) obtained from MD, \( \rho_{at} = \rho(1) \), and \( S = \rho(1)/\rho_s(T) \). The simulations were performed in a constant particle number, volume, and temperature ensemble. Usually, one would use a thermostat that directly controls the temperature such as simple velocity scaling or the Nosé-Hoover thermostat to control the system temperature. If we use these methods, however, the latent heat during droplet nucleation is unphysically extracted from the cluster cores. Therefore, in order to observe nucleation more realistically, target gas molecules were mixed with a carrier gas. This approach mimics that from experiments. In this case, the target gas molecules are those that nucleate, whereas the system temperature is controlled by the carrier gas using velocity rescaling.

Other simulation conditions used throughout this work include the Lennard-Jones (LJ) potential for target-target molecule interactions. The potential between target-carrier molecules and carrier-carrier molecules has only the repulsive term. The cutoff radius is 4.5 \( \sigma \). The total number of molecules is varied between simulations, but the ratio of target and carrier gas molecules was always fixed to be 1:1. The system sizes are initially fixed according to the initial supersaturation ratio, and three-dimensional periodic boundary conditions are applied, where the time step is 0.01 \( \tau \). After the whole system is initially equilibrated at \( T = 1.25 \epsilon / k_B \), the system temperature is changed to \( T = 0.67 \epsilon / k_B \), which is near the triple point, by velocity rescaling of the carrier gas molecule. The time at which the temperature was decreased is \( t = 0 \). Cluster sampling is performed at every 3.0 \( \tau \). The clusters are defined using the Stillinger criterion, which allocates molecules into the same cluster if the distance between them is smaller than \( r \leq r_c = 1.5 \sigma \). This value was chosen since it is the first minimum in the radial distribution function of an LJ liquid near the triple point. The number of molecules, initial supersaturation ratio and simulation time \( t_{end} \) differ for each simulation. These values are given in Table.2.

The simulations were performed using an application called the Framework for Developing Molecule Simulator (FDPS) created by the Particle Simulator Research team of RIKEN Advanced Institute of Computer Science(Iwasawa, 2016). This application enables users to make an MPI/OpenMP hybrid parallel simulation code by simply defining molecules and their interactions. FDPS decomposes the whole simulation domain dynamically in order to balance the calculation cost between available computational nodes. To run our MD simulation code with FDPS, we used 12 nodes, where the specifications are in Table.1.

<table>
<thead>
<tr>
<th>CPU</th>
<th># of cores</th>
<th># of threads</th>
<th>Frequency(base/max)</th>
<th>Memory</th>
<th>Interconnect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intel Xeon E5-2618L v3</td>
<td>8</td>
<td>16</td>
<td>2.30/3.40 GHz</td>
<td>DDR4 128GB</td>
<td>Infiniband FDR</td>
</tr>
</tbody>
</table>
Table 2: Results of each MD simulation. \( V(\sigma^3) \): System volume. \( N \): number of molecules. \( t_{end} \): simulation time. \( S_{int} \): Initial supersaturation ratio. \( S \): Supersaturation ratio. \( J_{MD}(\sigma^3 \tau^{-1}) \): Nucleation rate. \( n_{th}^* \): Thermodynamic critical cluster size. \( n_k^* \): Kinetic critical cluster size. \( \Delta G(n^*) \): Cluster formation free energy.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>( V(\sigma^3) )</th>
<th>( N )</th>
<th>( t_{end} (\tau) )</th>
<th>( S_{int} )</th>
<th>( S )</th>
<th>( J_{MD}(\sigma^3 \tau^{-1}) )</th>
<th>( n_{th}^* )</th>
<th>( n_k^* )</th>
<th>( \Delta G(n^*) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>281</td>
<td>1.0 x 10^6</td>
<td>2,000</td>
<td>14.0</td>
<td>6.91</td>
<td>7.35 x 10^{-8}</td>
<td>24</td>
<td>25-35</td>
<td>5.68</td>
</tr>
<tr>
<td>2</td>
<td>296</td>
<td>1.0 x 10^6</td>
<td>2,000</td>
<td>12.0</td>
<td>6.65</td>
<td>1.68 x 10^{-8}</td>
<td>27</td>
<td>40-45</td>
<td>6.46</td>
</tr>
<tr>
<td>3</td>
<td>314</td>
<td>1.0 x 10^6</td>
<td>4,000</td>
<td>10.0</td>
<td>6.21</td>
<td>1.70 x 10^{-9}</td>
<td>33</td>
<td>33-34</td>
<td>7.94</td>
</tr>
<tr>
<td>4</td>
<td>729</td>
<td>1.0 x 10^7</td>
<td>2,000</td>
<td>8.0</td>
<td>5.52</td>
<td>1.27 x 10^{-10}</td>
<td>35</td>
<td>33-36</td>
<td>9.41</td>
</tr>
</tbody>
</table>

RESULTS

Fig.1 shows some Snapshots of clusters at low supersaturation ratio condition. One can see few clusters in the large system.

In Table 2, a summary of the conditions and results for each MD simulation is presented. The supersaturation ratio is calculated from the average monomer density at the steady state, nucleation stage. At the same time, the nucleation rate \( J_{MD} \) is estimated using the threshold method counting the number of clusters larger than a given threshold value. One can see a tendency, where the nucleation rate decreases with the supersaturation ratio. Since monomers are the primary source of cluster formation, clusters are less likely to grow at low supersaturation ratio conditions.

The critical nucleus size \( n^* \) can be defined in two ways: the thermodynamic definition \( n_{th}^* \) and the kinetic definition \( n_k^* \). The former is obtained from the cluster formation free energy curve, and the latter is estimated from the cluster size change rate. The difference in the two critical nucleus sizes is small, and it also appears that the accuracy of \( n_k^* \) is dependent upon the simulation time or, more precisely, the number of samples recorded. Therefore, if one makes the simulation time longer, one can expect \( n_{th}^* \approx n_k^* \).

In Fig.2 (a), ratios of the nucleation rate \( J_{MD} \), measured by the threshold method, are presented. First, when compared with CNT, one can see that nucleation rates in the MD simulations, \( J_{MD} \), are almost eight orders of magnitude larger than the theoretical prediction of \( J_{CNT} \) using Eq. (2). Next, we input values obtained from MD simulations in Eq. (1), excluding the forward rates \( \beta(n^*) \). In this way, the nucleation rate \( J_{\beta} \), the difference is about one order of magnitude. Lastly, we used all values obtained from our MD simulations in Eq. (1), including the forward rates \( \beta(n^*) \). Using this result \( J_{k++} \), one can see that the agreement with \( J_{MD} \) is very good, within at least an order of magnitude.

The cluster formation free energy barrier estimated from MD simulations is presented in Fig.2 (b), together with the theoretical line. We set the horizontal axis to \((\ln S)^2\) instead of Eq. (3), so the relationship may be displayed proportionally. We can conclude that the free energy barrier becomes
smaller with increasing supersaturation ratio. However, the quantitative height of this barrier differs between MD and CNT analysis. The height of CNT free barrier is double that estimated from our MD simulations. CNT may overestimate the energy barrier, which could explain the 8 orders of magnitude difference in Fig.2 (a), which means there is some room for improvement in CNT.

Figure 2: (a) Ratios of MD nucleation rate, measured directly, $J_{MD}$, to that derived from the free energy, $J_{k^+}$, $J_\beta$, and CNT, $J_{CNT}$. The difference between $J_{k^+}$ and $J_\beta$ is that the latter does not include the forward rate term. (b) Cluster formation free energy barrier $\Delta G^*$. Values, as measured directly from MD simulations, $\Delta G^*$, and estimated by CNT, $\Delta G^*$, are plotted.

CONCLUSIONS

By conducting large scale MD simulations, we found that the nucleation rate using the values directly obtained from MD to the theoretical equation has good agreement with that obtained from the threshold method. In addition, kinetic analysis revealed that the cluster formation free energy from CNT was overestimated.

REFERENCES


PHOTOPHORETIC MOTION OF FRACTAL-LIKE SOOT AGGREGATES: NEW MICROPHYSICAL MODEL AND ATMOSPHERIC APPLICATIONS

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Keywords: BLACK CARBON, FRACTAL-LIKE PARTICLES, PHOTOPHORESIS.

INTRODUCTION

A unilaterally irradiated particle in a rarefied gas is affected by the photophoretic force. This force is of a radiometric nature and is the result of gas molecules interaction with the non-uniformly heated particle surface. To solve a photophoresis problem it is necessary to consider electromagnetic radiation absorbed by the particle, and to calculate the photophoretic force and velocity. Nowadays, the theory of longitudinal radiometric photophoresis for spherical homogeneous particles has found confirmation in experiments with model macroscopic particles and real aerosols for a complete set of determining parameters (Beresnev et al., 1993). The most essential photophoretic effects show carbonaceous aerosols well absorbing radiation practically in the all range of radiation wavelengths. The theoretical description of photophoretic motion of soot aerosols, as a rule, is carried out for the model of homogeneous spheres. However, the most part of soot atmospheric particles (black carbon) have a fractal-like structure, and we can expect essential changes of thermal and optical characteristics of these aggregates in comparison with homogeneous spheres.

This report summarizes analysis and estimations of the photophoretic effects for soot atmospheric aerosols on the basis of new microphysical model by Beresnev et al. (2014, 2015, 2016). In new model the mathematical formalism used in the model for homogeneous spheres by Beresnev et al. (1993) is kept at correct treatment of key parameters. The correct estimation of effective density and effective heat conductivity of fractal-like aggregates as equivalent spheres can be successfully executed on the basis of "thermal" model by Evans et al. (2008). The qualitative description of photophoretic motion of fractal-like soot aggregates it is possible to meet in many publications, however, the experiments supposing quantitative comparison with the theory are absent actually. Rare exceptions are the results received earlier by Karasev et al. (2004), and we address to the analysis of this experiment again.

The new model allows to carry out the estimations of photophoretic effects for soot aerosol in atmosphere similar with presented earlier by Beresnev et al. (2011, 2012) for homogeneous spheres. The analysis of received results shows that for fractal-like soot particles the essential photophoretic effects in stratosphere are important: the essential photophoretic vertical velocities, excess of photophoretic forces over gravity, possibility of a levitation of particles at certain altitudes in the middle stratosphere.

METHODS

The calculation of force and velocity of longitudinal radiometric photophoresis is based on the molecular-kinetic theory of this phenomenon (Beresnev et al., 1993). This theory is based on the solution of gas-kinetic model equation with the corresponding boundary conditions for the velocity distribution function on the particle surface, and covers the entire range of the Knudsen number $Kn$ ($Kn = l/R$, where $l$ is the mean free path of gas molecules) at arbitrary ratio between the thermal conductivities of the particulate matter and gas $\Lambda = \lambda_p / \lambda_g$, taking into account the optical and accommodation properties of the particle-gas system. The expression for the photophoretic velocity in the entire range of $Kn$ number can be presented in a form (Beresnev et al., 1993):

$$U_{ph} = -\frac{\pi}{2(8+\pi)} \frac{M_1}{\rho_0} \Phi(Kn, \Lambda, \alpha),$$
where $F(Kn, \Lambda)$ and $\Phi(Kn, \Lambda)$ are the functions of the $Kn$ number, dimensionless heat-conductivity ratio $\Lambda$, accommodation coefficients $\alpha$ of momentum and energy of gas molecules on the particle surface. The spectral photopheretic asymmetry factor $J_i$ is the basic result of solution of the electrodynamic problem of photophoresis (Beresnev and Kochneva, 2003). This factor is determined by the internal field in particle and depends on the magnitude of size parameter $\rho$ and complex refractive index $m$.

In experiments of Karasev et al. (2004) photophoretic motion of soot aggregates driven by a helium–neon laser beam is observed by the microscopic video system at standard temperature and pressure. Soot aggregates have been formed by benzene pyrolysis in a flow reactor, and the size of primary particles in aggregates was 40-200 nm. The fractal dimension for aggregates formed by benzene pyrolysis in DLCA regime was equal to $D_f=1.8$. Soot aerosol was injected to an optical cell at atmospheric pressure and room temperature. A focused He-Ne laser beam passed through the cell volume. Video observations showed that soot aggregates illuminated by the light of He-Ne laser moved in the direction of the beam (so-called positive longitudinal photophoresis). For each aggregate observed by the video system have been determined both photophoretic velocity at the fixed power of light beam of 2.5 W/cm$^2$, and equivalent mobility radius by Brownian motion for small aggregates. Comparison of experiment with the theory for homogeneous spheres has shown that this theory describes successfully experiment as qualitatively, and quantitatively, but it is necessary to interpret correctly key parameters used in calculations (see in detail in Beresnev et al., 2014).

The problem of estimations of the effective heat-conductivity ratio $\lambda$ for the fractal-like aggregates is actual for a number of reasons, and constructive results in this direction can be received, for example, using the method of effective homogenization (Evans et al., 2008). For our purposes we use further the dimensionless ratio $\Lambda = \frac{\lambda_{\text{eff}}}{\lambda}$, where $\lambda$ is the gas translational heat conductivity. On Fig. 1 the dimensionless heat-conductivity ratio $\Lambda$ calculated by the “thermal” model of Evans et al. (2008) for soot aggregates at various radius of primary particles $R_a$ and fixed heat conductivity of primary particles (microcrystalline graphite, $\lambda_a=50$ and 100 W/(mK)) in nitrogen at atmospheric pressure and room temperature is presented. It is clear, that the used model really predicts the expected values of $\Lambda$ in range 100-150 near to the found optimum of $\Lambda$ in experiment (see in detail in Beresnev et al., 2015).

On Fig. 2 the comparison of the new “photophoretic” theory for fractal-like particles with the unique experimental data by Karasev et al. (2004) is presented.

![Figure 1](image1.png)

*Figure 1 (at the left). Effective heat-conductivity ratio $\Lambda$ calculated by method of Evans et al. (2008) for soot aggregates at various radius $R_a$ and heat conductivity of primary particles $\lambda_a=50$ and 100 W/(mK).*

![Figure 2](image2.png)

*Figure 2 (on the right). The comparison of the new theory for fractal-like soot aggregates with experiment by Karasev et al (2004). Black circles – experiment; 1 – FLP-theory for primary particles radius $R_a=15$ nm; 2 – 20 nm; 3 – 30 nm; 4 – 40 nm. The heat conductivity of primary particles $\lambda_a=80$ W/(mK), fractal dimension of aggregates $D_f=1.80$, light beam intensity $I=2.5$ W/cm$^2$ (helium-neon laser with wavelength $\lambda=0.68$ μm).*
The new model allows to carry out the estimations of photophoretic effects for soot aerosol in atmosphere similar with presented earlier by Beresnev et al (2011, 2012) for homogeneous spheres. The analysis of received results shows that for fractal-like soot particles the essential photophoretic effects in stratosphere are important: the essential photophoretic vertical velocities, excess of photophoretic forces over gravity, possibility of a levitation of particles at certain altitudes in the middle stratosphere (see in detail in Beresnev et al., 2015).

Figure 3 (at the left). Photophoresis of fractal-like soot atmospheric particles in the field of short-wave solar radiation. Altitudes of possible localization of soot particles in stationary equatorial atmosphere. Blue and green lines – homogeneous spherical particles model at $A=5, \rho=0.165 \text{ g/cm}^3$ and $0.350 \text{ g/cm}^3$, correspondingly; red solid line – FLP-model at $D_f=1.80, \rho_s=2 \text{ g/cm}^3; R_a=20 \text{ nm}, \lambda_a=50 \text{ W/(mK)}$; black solid line – the same, but $\lambda_a=100 \text{ W/(mK)}$; red dash line – $R_a=40 \text{ nm}, \lambda_a=50 \text{ W/(mK)}$.

Figure 4 (on the right). Photophoresis of fractal-like soot atmospheric particles in the field of long-wave thermal radiation. Altitudes of possible localization of soot particles in stationary tropical atmosphere. Blue solid line – homogeneous spherical particles model at $A=5, \rho=0.165 \text{ g/cm}^3$; red line – fractal-like particles model at $D_f=1.80, \rho_s=2 \text{ g/cm}^3; R_a=20 \text{ nm}, \lambda_a=50 \text{ W/(mK)}$; black dot line – $R_a=20 \text{ nm}, \lambda_a=100 \text{ W/(mK)}$; green solid line – $R_a=40 \text{ nm}, \lambda_a=50 \text{ W/(mK)}$; brown solid line – $R_a=40 \text{ nm}, \lambda_a=100 \text{ W/(mK)}$.

CONCLUSIONS

In the new model for photophoresis of fractal-like particles the replacement of real soot aggregates by equivalent spheres with the mobility radius $R_m$ (defined on gyration radius $R_g$) is supposed. Effective density, heat conductivity and complex refractive index of equivalent spheres are defined from known characteristics of primary particles and fractal dimension of aggregate. The FLP-model is verified by comparison with reliable experimental data. Estimations of transport capabilities for soot particles photophoresis in the field of atmospheric radiation with the FLP-model demonstrate again (as well as for model of homogeneous spheres) the possibility of lifting and localization of soot particles at certain altitudes in the upper troposphere and stratosphere.

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REFERENCES


A NEW SETUP FOR THE STUDY OF ION-MOLECULE AND ION-PHOTON REACTIONS RELEVANT FOR AEROSOL SCIENCE

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Keywords: PHOTO IONISATION, ION-MOLECULE REACTIONS, NUCLEATION.

INTRODUCTION

Both negative and positive ions are constantly formed in the Earth’s atmosphere through various processes, including direct ionisation and other photo-induced reactions, and ions are consistently detected in aerosol field measurements (Hirsikko \textit{et al.}, 2011). Ions are believed to participate in atmospheric cluster formation, a process known as ion-mediated nucleation (IMN). Theoretical models have revealed that ions may play an important role in aerosol formation and that IMN rates are very sensitive to the ambient temperature (Yu, 2010). However, the significance of the role of ions for aerosol formation still needs experimental clarification.

We will present a novel experimental facility (XRING laboratory), that has been realised in connection with the ATRID2 synchrotron radiation facility (Møller \textit{et al.}, 2010), which allows the study of photo-absorption and photo-ionisation as well as ion-molecule reactions for isolated molecular species. We will discuss possibilities for using this facility in studies of atmospheric processes and nucleation in particular.

METHODS

The XRING laboratory is connected to the low energy synchrotron radiation facility ASTRID2 at Aarhus University, which provide a tunable photon beam in the energy range 7-200 eV and with intensities of $10^{12} - 10^{14}$ photons/s.

The XRING laboratory houses three experimental stations that enable a detailed view into photo-induced process and ion-molecule reactions by providing complimentary informations.

The first station allows photo-absorption and photo-ionisation cross sections of neutral species to be investigated with a standard gas-cell setup, where the photon beam from ASTRID2 is passed through a gas at relatively high pressure ($\sim 0.1$ Torr) and where the ionisation yield as well as the direct damping of the photon intensity are monitored.

The second station consist of a combined radio-frequency ion trap (Svendsen \textit{et al.}, 2013; Svendsen \textit{et al.}, 2014) operated under high-vacuum condition where ionisation (and ionisation plus dissociation) reactions of neutral and charged species can be studied by analysing the fragments emerging after photon irradiation. This station furthermore also allows studies of ion-molecule reactions.

The third station is a crossed photon-ion beam setup that allows for a more complete kinematical analysis of photon-induced reactions, since the individual fragments resulting from photo-absorption
(e.g. dissociation products) and photoionisation can be analysed with respect to charges and momenta.

CONCLUSIONS

For atmospheric processes, the facility could contribute with a bottom-up approach to analyse aerosol formation mechanisms, since selected elemental molecular reactions can be studied, and thus be complimentary to investigations for instance in smog chambers.

ACKNOWLEDGEMENTS

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REFERENCES

Hirsikko et al. (2011), Atmospheric ions and nucleation: a review of observations. Atmospheric Chemistry and Physics, 11, 2


Svendsen et al. (2013) Trapping ions from a fast beam in a radio-frequency ion trap: Exploring the energy exchange with the longitudinal radio-frequency field, Phys. Rev. A, 87, 4.

EXPLORATORY CLASSIFICATION OF AEROSOL MASS SPECTRA

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Keywords: CHEMOMETRICS, MASS SPECTROMETRY, AMS, CLUSTERING

INTRODUCTION

In a typical unit resolution time-of-flight mass spectrum, variables (mass-to-charge, m/z), are counted in the hundreds or thousands. Instruments such as the time-of-flight aerosol mass spectrometer (ToF-AMS) are able to produce such a spectrum in a matter of fractions of a second, although the result is usually averaged over several such extractions to yield a spectrum every few minutes. Over a period of a month such a measurement would still produce a set of data of ca. 10 000 spectra, each containing several hundred variables. To describe and interpret the underlying temporal changes in chemistry, statistical analytical techniques are required. The likes of the above described data set are a prime target for chemometric data reduction and classification techniques designed to reduce the amount of variables down to more humanely manageable numbers with minimal loss of information. Here we describe such a technique for unsupervised feature extraction and classification for AMS data.

METHODS

We studied an example set of 81 unit resolution aerosol spectra, obtained with an Aerosol Mass Spectrometer (AMS; Jayne et al., 2000). The samples each contained a characteristic mass spectra of air pollution episodes measured at the rural background station, SMEAR II, in southern Finland, during three measurement campaigns in 2008-2009. The pollution spectra were de-convolved from ambient measurements by a linear factor analytical model (Paatero, 1999), differentiating the pollution factors from the background aerosols.

For this work we tested the aptness of four dissimilarity metrics (Pearson correlation, dot-product cosine, squared Euclidean “distance” and Manhattan distance) for describing the (dis)similarity between the aerosol mass spectral samples. We conclude there are indeed differences between the metrics’ performances. Both ‘dot-product cosine’ and ‘Pearson correlation’ were found to produce similar, robust classification results, with ‘squared Euclidean’ dissimilarity providing satisfactory results. The classification solution quality was measured using the silhouette metric, was used for evaluating the solution quality and the effect of scaling in data pre-processing.

We also explored the effects of applying non-uniform weight distribution to the mass spectral variables, as is commonly done and advocated for in many mass spectrometric applications outside of aerosol sciences (Stein and Scott, 1994).

Comparing to uniform weight distribution we find ion mass based weighting for data variables markedly enhances the aerosol chemotype classification while signal intensity based (inverse) weighting appears detrimental to it in our case of normalized AMS spectra.
RESULTS AND CONCLUSIONS

We find that even a simplistic, unsupervised, classification algorithm such as k-means can, with optimized similarity metric and data weighting, reproduce classical organic aerosol speciation schemes, and differentiate between aerosols of similar oxidation state, and separate organic aerosol sub-species even in classically difficult cases where the differences are subtle (e.g. traffic generated aerosol and cooking aerosol).

Based on this (albeit limited) study, we would like to encourage metric and variable weight distribution optimization in connection to any data analytical tasks involving aerosol mass spectra classification or algorithm-based identification. We find that Pearson correlation seems a suitable metric for identification and classification AMS mass spectra, although some theoretical considerations would seem to favour dot-product cosine metric instead. The two seem to produce almost identical results in our tests. We also recommend exploring ‘mass scaling’ as a basis of weight distribution among variables, as in our case it does markedly enhance aerosol classification to aerosol chemotypes.

From the test data we identified 5 to 7 recurring pollution types, including sawmill (secondary) organic aerosol, anthropogenic highly oxidized, long-range transported pollution, fresh traffic related hydrocarbon-like aerosol, and cooking aerosol. Additionally we detected and classified three “outlier” pollution groups with high amine contents.

We hope these promising results pave way for a more automated and objective, machine driven aerosol classification methodologies to come in the future. Further background, discussion and results of this work are available in the online manuscript, currently under review in Atmospheric Chemistry and Physics Discussions (Äijälä et al., 2016).

ACKNOWLEDGEMENTS

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REFERENCES


COMPUTATIONAL PREDICTION OF SALTING IN AND SALTING OUT EFFECTS

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Keywords: Aerosols, Organics, Salting in/out, COSMO-RS.

INTRODUCTION

Atmospheric aerosols typically contain an inorganic component, such as sea salt and ammonium sulfate. These salts affect the solubility of organic molecules. The solubility of neutral organic solutes in salt water may be quantitatively described by the Setchenow relationship:

$$\log \left( \frac{S_0}{S} \right) = K_S c_S$$

where $S_0$ and $S$ are the solubilities of solute in pure water and salt solution. Positive values of the salting constant $K_S$ indicate a salting out effect, i.e., the salt lowers the solubility of the organics, and negative values indicate salting in. The salt concentration, $c_S$, used in this study is 0.5 mol/l, which is a typical seawater salt concentration. In this work we have computationally studied salting in/out of various organic compound in several different salt solutions.

METHODS

We have calculated salting constants using a method based on an electrostatic theory of locally interacting molecular surface descriptors and statistical thermodynamics, COSMO-RS ([Eckert and Klamt, 2002]). Termodynamical properties of liquid systems are calculated from quantum chemistry based molecular interactions, and no system-specific experimental parameters are needed. COSMOTHERM ([Eckert and Klamt, 2014]) is a commercial program based on the COSMO-RS method. We have carried out quantum chemistry calculations (to produce cosmo-files) on the TZVPD-FINE level, which is the highest-quality calculation method currently available for COSMO-RS simulations.

RESULTS AND CONCLUSIONS

All the salting constant values for the studied organic-salt-pairs are presented in the figure 1. From previous studies (See e.g. Endo, 2012) we know that COSMOTHERM underestimates the salting in effect and overestimates the salting out effect. Our results agree with previous studies.

Systems containing large organic salts, Pro4N⁺ or Et4N⁺, are predicted to salt in most of the studied organics. If we then look at the Cl- and Br- solutions, apart from few exceptions, the order of $K_S$ values is the following: Pro4N⁺ < Et4N⁺ < Met4N⁺ < Na⁺ ≈ NH4⁺.

If we consider the solutions of NH4⁺ and Na⁺ cations, the values of the salting constants of the organics appear in pairs: C₂O₄²⁻ and SO₄²⁻ solutions salt out more strongly than Cl⁻ and Br⁻ solutions in most of the cases.
Figure 1. We calculated salt-organic-pair specific salting constant, $K_s$ for 24 organic molecules in 14 different salt solutions.

The $K_s$ value of the system is affected by the interactions between the water molecules and the salt ions, and the interactions between the organic molecule and the salt ions. Strong interactions between a water molecule and an ion decreases the solubility of an organic solute, i.e. increase the cohesion energy of the solute molecule. The screening charge distributions of large organic salt ions ($\text{Pro4N}^+$, $\text{Et4N}^+$) are, however, complementary with the organic molecules charge distributions, causing a salting in effect.

ACKNOWLEDGEMENTS

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REFERENCES

THE EFFECT OF PARTICLE ACIDITY ON α-PINENE SOA FORMATION

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Keywords: α-Pinene, Secondary Organic Aerosol, Acid Catalysis, Heterogeneous Reactions

INTRODUCTION

The effect of aerosol acidity on Secondary Organic Aerosol (SOA) formation is one of the open scientific questions in the literature. Acid-catalyzed heterogeneous reactions such as hydration, hemiacetal/acetal formation, polymerization, and aldol condensation have been proposed to form SOA (Jang et al., 2002). The presence of acidic aerosol particles has been reported to enhance the reactive uptake of certain gas-phase species such as glyoxal (Liggin et al., 2005). However, other studies have suggested that reactions may be thermodynamically unflavored and possibility insignificant in the ambient atmosphere (Barsanti and Pankow, 2004). In contrast, recent kinetic studies have demonstrated that particle acidity strongly affects the reactive uptake of isoprene epoxydiols (Gaston et al., 2014). Field studies have shown mixed results with some studies showing an acid-catalysis effect and other studies showing no apparent evidence.

This study aims to improve our current understanding of the effect of particle acidity on SOA formation from laboratory studies of the photooxidation of α-pinene under both high and low NOx conditions. Chamber studies were performed under low organic aerosol mass concentrations and moderate relative humidity, which are representative of ambient conditions.

METHODS

Photooxidation experiments were performed in a 2m³ Teflon chamber (Whelch Flurocarbon) enclosed in an aluminum support. Twelve black light lamps (model F32T8/350BL, Sylvania) were used as the irradiation source with intensity peaking at approximately 350 nm. Table 1 lists the experimental conditions for each experiment.
Table 1. Initial conditions and SOA yields from experiments under high and low NOx conditions.

<table>
<thead>
<tr>
<th>pH</th>
<th>Temp°</th>
<th>RH (%)</th>
<th>Seed (μg m⁻²)</th>
<th>NO (ppb)</th>
<th>α-pinene (ppb)</th>
<th>ΔHC (μg m⁻³)</th>
<th>ΔM₀ (μg m⁻³)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.31</td>
<td>24–31</td>
<td>47–79</td>
<td>4.4</td>
<td>66</td>
<td>15.9</td>
<td>84.2</td>
<td>3.5</td>
<td>42 ± 0.1</td>
</tr>
<tr>
<td>-1.50</td>
<td>24–30</td>
<td>58–34</td>
<td>8.4</td>
<td>69</td>
<td>17.6</td>
<td>93.4</td>
<td>5.2</td>
<td>56 ± 0.1</td>
</tr>
<tr>
<td>-1.66</td>
<td>26–33</td>
<td>58–33</td>
<td>6.3</td>
<td>68</td>
<td>13.6</td>
<td>71.8</td>
<td>4.7</td>
<td>66 ± 0.1</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Figure 1 illustrates the SOA yields as a function of organic mass concentrations for experiments under seed particles with varied acidity conditions under high and low NOx conditions.
The SOA yield (4.2–7.6 %) measured early in each experiment increased nearly linearly with the increase in particle acidity under high-NOx conditions. In contrast, the SOA yield (28.6–36.3 %) was substantially higher under low-NOx conditions, but its dependency on particle acidity was insignificant. Under high NOx conditions, the SOA yield decreased gradually with the increase in organic mass in the initial stage (approximately 0–1 h), which is likely due to an inaccessibility to the acidity over time with the coating of α-pinene SOA, assuming a slow particle-phase diffusion of organic molecules into the inorganic seeds. We also performed experiments where we waited to add the acidic seed until later in the photooxidation. The formation of later-generation SOA was enhanced by particle acidity even under low-NOx conditions when introducing acidic seed particles after α-pinene photooxidation, suggesting a different acidity effect exists for α-pinene SOA derived from later oxidation stages. This effect could be important in the atmosphere under conditions where α-pinene oxidation products in the gas-phase originating in forested areas (with low NOx and SOx emissions) are transported to regions abundant in acidic aerosols such as power plant plumes or urban regions.

The fraction of oxygen-containing organic fragments (C_{x}H_{y}O_{z}^{+} 33–35% and C_{x}H_{y}O_{z}^{+} 16–17%) in the total organics and the O/C ratio (0.52–0.56) of α-pinene SOA were lower under high-NOx conditions than those under low-NOx conditions (39–40, 17–19, and 0.61–0.64 %), suggesting that α-pinene SOA was less oxygenated in the studied conditions. The fraction of nitrogen containing organic fragments in the total organics was enhanced with the increases in particle acidity under high-NOx conditions, indicating that organic nitrates may be formed heterogeneously through a mechanism catalyzed by particle acidity or that acidic conditions facilitate the partitioning of gas-phase organic nitrates into particle phase. The results of this study suggest that inorganic acidity has a significant role to play in determining various organic aerosol chemical properties such as mass yields, oxidation state, and organic nitrate content.
REFERENCES


A THERMODYNAMIC DESCRIPTION FOR THE CONTINUOUS DELIQUESCENCE OF ATMOSPHERIC AEROSOL PARTICLES

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Keywords: deliquescence, nucleation, hygroscopicity, Köhler theory.

INTRODUCTION

The phase state of atmospheric particulate is important to atmospheric processes, including understanding aerosol radiative forcing in a climate context (Davis et al., 2015). That said, precise phase behavior is difficult to quantify in the atmospheric context and the classical Köhler representation (Köhler, 1936; Seinfeld et al., 2016) of hygroscopic growth presumes a jump transition between dry and solvated particles or a gradual transition taking into account limited solubility (Bilde et al., 2004). We propose here a revised and more detailed approach to understanding the transition from solid soluble particles to liquid solution droplets.

At a certain deliquescence relative humidity below the saturation point of water vapor, salt particles are observed to dissolve resulting in water droplets of brine composition. This deliquescence phenomenon is implicit in Köhler theory which describes the stability of solution droplets, but it does not capture observations of pre-condensation, or particle growth below deliquescence. Instead of the sudden transition predicted by Köhler theory, we model a salt particle being gradually engulfed and dissolved by a growing brine layer. The newly represented thermodynamic equilibrium may have implications in mixed phase systems and other climate relevant contexts.

![Diagram](image-url)

Figure 1: Schematic of an idealized solvating atmospheric particle, with the electrolyte distribution and resulting interfacial potential near the salt/solution interface illustrated.
Methods

Although the transition from solid salt to liquid brine solution may proceed quickly, it is important to consider whether or not there exists any intermediate state(s) of importance. Here we consider whether a particle may be wetted by a thin film prior to deliquescence and ask what forces stabilize or destabilize such a system. Reformulating atmospheric particle dissolution as an interfacial problem, rather than a bulk thermodynamic problem, leads to the system postulated in Fig. 1, where a charged salt particle is engulfed and dissolved by a brine layer. In order for the interfacial system to endure it must yield some energetic benefit that can be captured by minimizing the global free energy of the system. Thus in addition to the bulk free energies tacit in Köhler theory (Raoult's law and Kelvin effect), an interfacial contribution must be included. Thus we construct a theoretical model of the liquid layer thickness $l$ using Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin et al., 1941; Verwey et al., 1948; Luo, 2007), which assesses the balance between short and long range intermolecular interactions, and has been used to great success for thin films.

Conclusions

The new theory yields a smooth meta-stable transition from solid to aqueous phase atmospheric particles (Fig. 2, red line), while reducing to the classical Köhler formulation (Fig. 2, blue line) once the particle has fully dissolved and the stabilizing interfacial forces have vanished (Fig. 2, yellow dash). Comparison with measurement data for 1:1 electrolytes shows good agreement both above and below the deliquescence transition (Fig. 2, Biskos et al., 2006 data), but the theory is general in that depending on the intermolecular force balance, the surface of any soluble material containing atmospheric particle may potentially ‘pre-deliquesce’.

Figure 2: The evolution of the individual terms of the refined Köhler equation accounting for limited solubility as well as an interfacial contribution are shown for a solvating 3 nm NaCl particle. It can be seen that the intermolecular interactions are very short range (orange curve) and responsible for particle growth at low humidity (red curve).
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REFERENCES


WORK OF FORMATION OF CAESIUM HYDROXIDE CLUSTERS DETERMINED BY GUIDED MITOSIS

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Keywords: Free energy computation, Molecular dynamics, Molecular clusters, Nuclear aerosols.

INTRODUCTION

Metal hydroxides are of technological significance in many applications (Chroneos et al., 2006). In particular, a key hazard from a severe accident in a water-cooled nuclear reactor is the release of radioactive caesium which may react with steam to form high temperature caesium hydroxide vapour. As this vapour flows away from the molten core it will cool and condense. This study is concerned with the the formation of caesium hydroxide aerosol by nucleation from this vapour phase. We employ the Jarzynski equality to extract the nucleation barrier from nonequilibrium molecular dynamics simulations, using the code LAMMPS (Plimpton, 1995).

METHODS

The first stage in molecular dynamics modelling is the selection of an appropriate potential. We followed Chroneos et al. (2006) in representing the interatomic potentials of metal hydroxides by Coulomb interactions supplemented by short-range Buckingham terms. The parameters in the potential were found by fitting simulations of the crystal structure to the known lattice parameters for CsOH (Jacobs et al., 1987). CsOH has an orthorhombic phase at temperatures below 500 K and a cubic phase at higher temperatures. The simplicity of our potential did not allow a match of the lattice parameters of both phases simultaneously but our attention is focussed on modelling the high temperature cubic phase, and we adjusted the potential to reproduce the lattice parameters for this phase to within 2%. The model material had a melting point of around 650 K, slightly higher than the experimental value for CsOH of 620 K.

The potential was then used to calculate the free energy change, or thermodynamic work, of cluster formation using the mitosis method developed by Ford and co-workers (Tang and Ford, 2015; Lau et al., 2015; Parkinson et al., 2016). The method relies on the Jarzynski equality:

\[ \langle \exp(-W / kT) \rangle = \exp(-\Delta F / kT) \]

where \( W \) is the mechanical work performed during the manipulation of the Hamiltonian of a system and \( \Delta F \) is the associated change in free energy between the initial and final equilibrium states. The angled brackets indicate an average over many realisations of the process.

Equation (1) was applied as follows. An ensemble of equilibrium clusters of \( 2^n \) molecules at temperature \( T \) was set up with the constituent atoms attached to two fictitious “guide particles” by weak springs (half the atoms attached to each guide particle). The spring constants were sufficiently small that the equilibrium structure of the cluster was not significantly disturbed. The temperature was maintained by a Langevin thermostat. The cluster was then separated into two clusters, each of size \( 2^{n/2} \), by the following 5-stage procedure:
Stage 1: the guide particles were moved apart at constant velocity through a distance \( d_i \);
Stage 2: the guide particles were held stationary and the springs strengthened, pulling the cluster apart;
Stage 3: the guide particles were moved further away with the same velocity as before;
Stage 4: with the guide particles still moving, the spring constants were reduced to their initial value;
Stage 5: the guide particles continue to move, with the spring constants equal to their initial value.

This procedure was adopted in preference to simpler protocols since it tends to avoid abrupt irreversible “snapping” events which lead to poor statistics (Parkinson et al., 2016). The procedure was repeated many times (typically 1000), and the total work done recorded for each trajectory. Four such realisations are shown in figure 1. All simulations were performed at a temperature of 1000 K.

![Graph](image1.png)

Figure 1: variation of work done against time elapsed during the mitosis of four CsOH octomers. The dashed lines indicate the 5 stages in the procedure, as discussed in the text. The performance of work in stages 1 and 2 corresponds to the breaking of intermolecular forces and strengthening of tethers, while the return of work in stage 4 arises from tether loosening.

![Graph](image2.png)

Figure 2: histogram of work performed during the mitosis of an octomer (1000 trials) showing a two-peaked distribution.
Figure 3: total free energy change in the splitting of an octomer into two tetramers by mitosis, as a function of total simulation time. The error bars are estimated by dividing the 1000 values of \( W \) into 10 equal groups and applying Eq. (1) to each group.

The point of using Eq. (1) is that a broad distribution of \( W \) can be reduced to a specific value of the associated free energy change \( \Delta F \). Nevertheless, accuracy in computing the free energy change from limited simulation data is improved if the work distribution can be narrowed. However, for some ranges of parameters, anomalously high values of \( W \) were found, e.g. see figure 2. The reason for their appearance was investigated. It was found that these cases related to situations where a hydrogen and an oxygen atom attached to different guide particles happened to form a hydroxyl group which was later pulled apart when the spring constants increased, releasing a large amount of stored energy as heat. The method works best when the mechanical separation of the cluster is conducted as gently as possible, so we restricted our simulations to ranges of parameters which avoided generating these costly trajectories.

The resulting values of \( W \) were then used in Eq. (1) to determine \( \Delta F_{\text{min}} \), the free energy difference between a tethered cluster containing \( N=2^3 \) molecules and two tethered clusters each of size \( N/2 \). This free energy difference is not simply \( F(N)-2F(N/2) \), where \( F \) is the total free energy of an untethered molecular cluster, as there are additional terms relating to the indistinguishability of the molecules and the fixing of the centres of mass in the simulations, see Lau et al. (2015); however, these terms can be calculated in a straightforward manner. It is then possible to determine the effective surface free energy \( F_s(N) \) of dimers, tetramers, octamers, etc. For large droplets, this quantity should converge to the planar surface tension multiplied by a notional cluster surface area, and it is a key ingredient in nucleation theory (Ford (1997)).

Furthermore, a formula can be derived for “uneven mitosis” to relate, for example, the surface free energy of a 12-cluster to that of the octomer and tetramer. Values obtained depend on the time over which the separation takes place, although the dependence is weak (provided it is not too short), as can be seen in figure 3.

The thermodynamic potential associated with cluster growth and evaporation \( \phi(N) \), which can also be referred to as the thermodynamic work of cluster formation, is related to the surface free energy \( F_s(N) \) according to

\[
\phi(N) = F_s(N) - NkT \ln \rho_s / \rho_v,
\]

where \( \rho_s \) is the molecular number density of the precursor vapour (assumed to behave as a perfect gas), and \( \rho_v \) is the saturated vapour density. The difference \( \Delta \phi = \phi(N) - \phi(1) \) is commonly (if loosely) referred to as the nucleation free energy barrier that controls the kinetics of the emergence of droplets from the vapour. It should be noted that the nucleation barrier \( \Delta \phi(N) \) does not depend on saturated vapour density; the latter is only required for the evaluation of the surface free energy \( F_s(N) \).
Figure 4: nucleation barrier for CsOH cluster formation, in units of $kT$, vs size in CsOH molecules.

For $\rho > \rho_s$, $\Delta \phi(N)$ has a peak at $N^*$, which can be interpreted as the critical size above which growth becomes increasingly likely. Figure 4 illustrates such a case with $\rho_s=1.45\times10^{23}$ m$^{-3}$, corresponding to a highly supersaturated vapour (the experimental saturated vapour density for CsOH at 1000 K is around $1.45\times10^{23}$ m$^{-3}$) and consequently a fairly low nucleation barrier.

CONCLUSIONS

The mitosis method is a promising approach for determining the nucleation free energy barrier for liquid-like clusters of metal hydroxides such as CsOH. It is based on nonequilibrium molecular dynamics simulations of cluster separation, interpreted using the Jarzynski equality. We have identified a number of aspects that need careful attention for these systems, particularly the need to avoid costly realisations where the external work is performed against intramolecular rather than intermolecular forces. We have noted that identifying the nucleation barrier need not require the evaluation of the saturated vapour density. Current work is focussed on extending the calculations to larger clusters, more representative of those likely to be important in practical situations.

REFERENCES


CONTROLLING NUCLEATION RATES WITH PATTERNS OF IMPURITIES

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Keywords: Heterogeneous Nucleation, Seed Geometry, Rate Calculation, Ising Model.

INTRODUCTION

The occurrence of a first-order phase transition is usually related to heterogeneous nucleation, where the new stable phase forms due to the presence of impurities in the metastable phase, i.e. due to contact with an external surface. It could be shown via computer simulations that the presence of even smallest impurities enhances the nucleation rate dramatically (Sear, 2006). While it could be revealed that the size of the heterogeneity increases the rate exponentially, there have not been made any studies about the influence of its shape yet.

Our aim is therefore to explore the consequences for the system when changing the shape of the heterogeneity while keeping its size unaltered. Particularly, we are interested in finding a functional correlation between the nucleation rate and the geometrical parameters which describe the pattern of the heterogeneity. This is significant for practice as it puts us into the position to control the rates of nucleation knowing its dependence from the spatial distribution of the impurities.

METHODS

Figure 1: A snapshot from the simulation model. The lattice size is $l \times l = 20 \times 20$ spins. White squares represent the starting spin configuration of $-1$, red squares those with $+1$, and the black sites stand for the quenched spins with value $+1$. The above configuration was reached after 50 cycles at the temperature of $kT/J=1.15$.

We study heterogeneous nucleation by considering one of the best tested simple but nontrivial models of Statistical Mechanics which shows a first-order phase transition, namely the two-dimensional Ising model (Chandler, 1987). Our simulation model is a square lattice with $l \times l$ spins with periodic
boundary conditions and nearest neighbour interactions. The Hamiltonian of the system is given by

$$H = -J \sum_{\langle ij \rangle} s_i s_j,$$

where $J$ is the coupling constant, $\langle ij \rangle$ represents a sum over nearest neighbours and $s$ the spins which can assume the values $\pm 1$. In this case we are neglecting the external magnetic field which would add an additional term $-h \sum_i s_i$ but where the field $h$ would just distort our problem, in adding extra conditions beside the point. For temperatures below the critical temperature a spontaneous symmetry breaking occurs and the system exists either in a predominantly spin-up or spin-down state. In this specific case it is interesting to see the influence of quenched spins, spins which do affect their neighbours through the coupling constant, but cannot flip themselves. Setting them to an initial value means that these frozen spins keep their value over the whole simulation time. See Fig. 1 for a visualization of the applied model. The three quenched spins are positioned at arbitrary lattice sites, showing the high capability of building clusters in their vicinity. We have chosen a temperature well below the critical temperature of $kT_c/J = 2.27$ for our simulation runs, in order to focus only on the correlation between impurity pattern and nucleation rate. In this way we suppressed fluctuation effects closer to $T_c$, where the predominance of the two phases was less pronounced. After several trial runs the value of $kT/J = 1.15$ turned out as the best target value in observing phase transitions in our system.

To simulate the 2D Ising model we used Importance Sampling by applying the Metropolis-Hastings algorithm (Metropolis et al., 1953). One Monte Carlo step (MCS) consisted of one entire sweep where $20 \times 20$ spins were randomly chosen and evaluated as to an energetically favourable configuration. The phase transition was defined by reaching the new stable phase in which the relation for the number of new "spins" $n_{new} \geq 9 \times n_{old}$ was met.

RESULTS

![Figure 2: The nucleation rate as function of the summed distance between 3 impurities. Each point represents a rate estimate for a particular configuration of impurities on the lattice. Since the case $w = 3$ represents a triangle on a torus, the minimum perimeter can be calculated. The statistical uncertainties were smaller than the point size. The maximum perimeter a triangle can take on a $20 \times 20$ lattice with periodic boundary conditions is equal to 34.14 in units of lattice sites.](image)
Figure 3: Influence of the spatial distribution of impurities on the nucleation rate. In this set of simulation runs we kept one impurity on the lattice position (x/y) 0/0, another on the position (x/y) 10/10 and allowed the third one to step through all 400 positions of the whole 20 x 20 lattice. In each position the nucleation rate was computed, leading to a striking three-dimensional function. The two extrema represent the cases in which the position of the third impurity was identical with one of the other two, leading to the case of w = 2 and hence to a significantly smaller rate.

The following results for the case of w = 3 impurities into the system were obtained under the same simulation methodology, permitting therefore to be analyzed as a whole. The procedure was similar, just the spatial arrangement of these 3 impurities were varied. All nucleation rates are normalized by this number of impurities and given in units of lattice cycles of the system.

Fig. 2 shows the functional dependence of R on the perimeters of the impurity triangles. The perimeter is given by the sum of the three shortest distances between these three points on the torus. All different quenched spin configurations were investigated. As outcome we notice a strictly monotonically increasing dependence of R on the perimeter of the impurity triangle. In the range of highest perimeters there is then notable a plateau in the function, which may mean that beyond this distance the impurities do not feel each other any more. Even if the difference in the rates is very modest with a factor of just 1.7 between lowest and highest value, the functional relationship is yet clearly visible. The case of this small variations is in fact due to the circumstance that we used higher simulation temperatures, in order to save computational effort.

Additionally, it is an other striking feature of this computational outcome, that the graph shows clearly visible bifurcations. We can observe a remarkable main branch, on which most of the values concentrate. In addition to the main branch also other smaller branches are visible, each with its own distinct distribution of data points, and hence clearly identifiable. Between these single branches lies just empty space with no values left.

Fig. 3 gives a different graphical impression of the functional relationship discussed. The plot shows the dependence of R on the position of just one impurity, while the two others were held fixed, one in the corner and one in the centre. The functional dependence of the form \( A \sin(Bx + C) \) is well visible for increasing distances from each of the other two impurities. It can be clearly seen that the transition from \( w = 3 \) to \( w = 2 \) is continuous. Therefore, the relationship \( R(w) \) as examined in the previous autor's work (Sear, 2006) can also be rewritten as a relationship \( R(D) \) by only the distance of these impurities. The case of a smaller impurity number \( w \) is then obtained as limiting case in this relationship, by simply setting the concerning impurity distance to 0. I.e., it is possible to generalize \( R(w) \Rightarrow R(D) \), where a variation in \( w \) can simply be written as vanishing corresponding distance. Since this principle is valid only for \( w = 3 \), the search of other parameters...
seems to this effect even more important.

CONCLUSIONS

We performed Monte Carlo simulations of an Ising model with quenched spins, examining the influence of microscopic impurities on the nucleation rate. We could show that the nucleation rate does not only depend on the number of impurities within the system, but in a very profound way also on the associated pattern. We found a towards a limit strictly monotonically increasing dependence of the nucleation rate on the mean distance between the impurities. Furthermore, there were several distinct branches visible in a scatter diagram of the simulation data. The theoretical fact that a heterogeneity has even more influence if its surface is larger was confirmed in the simulation. If the case of the flat function curve after an explicit value $D_{\text{crit}}$ can be confirmed, then the by former authors revealed dependence of the nucleation rate on the size of the heterogeneity is valid only for the ranges of small distances $D$.

ACKNOWLEDGEMENTS

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REFERENCES

Zeldovich J.B. 1943, Acta Physicochimica USSR, **18**, 1
BOUNDARY LAYER NEW-PARTICLE FORMATION AND ROLL VORTICES

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Keywords: new-particle formation, planetary boundary layer, horizontal roll vortices, airborne aerosol measurements.

INTRODUCTION

New-particle formation (NPF) is a common phenomenon in the continental boundary layer and an important source of climatically relevant aerosol particles (Kulmala et al., 2013). Local scale (1–10 km) variation has been frequently observed in the number concentration of freshly formed particles even inside the well-mixed boundary layer over fairly homogeneous land areas (Väänänen et al., 2016). Understanding the processes behind the variation is necessary in order to reduce the uncertainties in current models and climate predictions.

We analyzed colocated airborne and ground-based measurements of aerosol particles and meteorological parameters. The aim was to identify and characterize specific locations inside the boundary layer where the nucleation mode particles had an increased number concentration and to explain this variation in aerosol concentration.

METHODS

The measurements took place in a rural boreal forest environment in southern Finland. An instrumented Cessna 172 light airplane was used in six intensive measurement campaigns during the years 2013–2015 (Väänänen et al. 2016). A Zeppelin NT research airship performed measurements during the spring 2013 (Manninen et al. 2017). The airborne measurements were flown in the vicinity of the SMEAR II (Station for Measuring Ecosystem–Atmosphere Relations; Hari and Kulmala, 2005) field station located in Hyytiälä (61°51’N, 24°17’E), and were complemented by the station’s extensive aerosol measurements.

Key aerosol instruments onboard the Cessna airplane were a TSI 3776 ultrafine condensation particle counter (>3 nm particle number concentration) and a homemade scanning mobility particle sizer (10–400 nm particle number-size distribution). The key aerosol instrument onboard the zeppelin was a neutral cluster and air ion spectrometer (Manninen et al. 2009, Mirme et al. 2010; 2–42 nm particle number-size distribution and 0.8–42 nm ion number-size distribution) manufactured by Airel Ltd. These instruments allowed us to obtain the nucleation mode particle concentration in the size range 3–20 nm.

The airplane measurements consisted of roughly 20–40 km long flight legs flown perpendicular to the mean wind at different altitudes, scanning the boundary layer and the lower free troposphere. An example flight track is illustrated in Figure 1. The zeppelin measured helical vertical profiles over a smaller area inside the boundary layer. The measurement flights were done during daytime between morning and afternoon.

In addition to the aerosol measurements, various meteorological parameters (temperature, relative humidity and wind) were measured from the aircrafts and the SMEAR II station. Mesoscale meteorological features were identified from weather radar scans and from satellite images.

RESULTS AND CONCLUSIONS

We found out that the aerosol number concentrations were elevated in particular locations inside the boundary layer. We were able to connect this feature to mesoscale circulation inside the boundary layer, namely to roll vortices (e.g. Etling and Brown, 1998). The roll vortices are large systems of horizontally...
aligned side-by-side helical circulations inside the planetary boundary layer. The rolls were identified from mast and airborne wind measurements, nearby weather radar measurements and satellite images of cloud streets. The elevated aerosol number concentrations were likely caused by enhanced NPF at the top of the rolls.

Based on our observations the roll enhanced NPF was a frequent phenomenon. The nucleation mode number concentration could increase 2–10 fold compared to the surroundings and the freshly formed particles seemed to grow at a similar rate with the regional NPF event particles. Extrapolating these results to regional scale means that the roll enhanced NPF could considerably increase the aerosol particle number concentration in the boundary layer above the boreal forest.

Our observations are supported by previous studies. Easter and Peters (1994) showed numerically that various flows and fluctuations in the atmosphere, including roll vortices, could enhance nucleation rate. Buzorius et al. (2001) observed that NPF events often coincided with the occurrence of rolls. The likely reason why the rolls can enhance the NPF was also identified in these studies. Namely the rolls can efficiently transport condensable vapors and clusters to the top of the boundary layer where nucleation and cluster activation becomes more favorable due to mixing over the capping inversion, decreased temperature and reduced condensation/coagulation sink.

Figure 1. The locations of Tampere-Pirkkala airport and Hyytiälä along with a flight track flown on August 13, 2015.

ACKNOWLEDGEMENTS

This work was supported by the Office of Science (BER), U.S. Department of Energy. This research has been funded by the ERC-Advanced “ATMNUCLE” (grant no. 227463), the Academy of Finland (Center of Excellence project no. 272041), the Eurostars Programme under contract no. E!6911 and the European Commission under the Framework Programme 7 (FP7-ENV-2010-265148), and the European Union’s FP7 capacities programme under ACTRIS (grant no. 262254), and Horizon 2020 research and innovation programme under ACTRIS-2 (grant no. 654109). In addition, this work was supported by CRAICC and the Swedish Research Councils.

REFERENCES

COMBINED EFFECTS OF BOUNDARY LAYER DYNAMICS AND ATMOSPHERIC CHEMISTRY ON AEROSOL COMPOSITION DURING NEW PARTICLE FORMATION PERIODS

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Keywords: BOUNDARY LAYER DYNAMICS, NUCLEATION, ATMOSPHERIC CHEMISTRY, AEROSOL MASS SPECTROMETRY, ELVOCs

INTRODUCTION

Nucleation events are frequently observed on a global scale (Kulmala et al., 2004). New particle formation depends on the gas-phase species emitted and their subsequent processing in the atmosphere. When emitted at the land surface, they enter into the planetary boundary layer (PBL), which is characterized by strong turbulent motions that are largely influenced by the underlying land surface and the free troposphere on top of it. PBL dynamics affect the processing the aerosol precursor species and the partitioning into the aerosol phase of their low-volatility reaction products.

This work presents characterization results of atmospheric aerosols in accordance with the PBL depth development by using a combination of several mass spectrometry in a boreal forest environmental in Finland. We systematically investigated the effects of (1) PBL development, (2) atmospheric chemistry and (3) aerosol entrainment from the free troposphere on the observed aerosol physicochemical properties before and during the nucleation events.

METHODS

The measurements were carried out at SMEAR II (Station for Measuring Forest Ecosystem-Aerosol Relations) in Hyytiälä forestlands in Southern Finland (61° 51′ N, 24° 17′ E) during 2nd April—10th July, 2014 (Hari and Kulmala, 2005). Real-time measurements of particle mass concentrations, chemical composition and size distributions were conducted using a soot particle aerosol mass spectrometer (SP-AMS) (Onasch et al., 2012). The SP-AMS is a standard Aerodyne high resolution time-of-flight AMS equipped with an intracavity laser vaporizer (1064nm), in addition to the tungsten vaporizer used in a standard AMS (DeCarlo et al., 2006). During the campaign SP-AMS was operated at 5-min saving cycles alternatively switching between El-mode and SP-mode.

The AMS data were processed using standard Tof-AMS Data Analysis Toolkit. Further analysis was performed by applying Positive Matrix Factorization (PMF) technique on the high-resolution mass spectra (Paatero and Tapper 1994; Ulbrich et al. 2009). The time series and errors of NO\(^+\) and NO\(_2\)\(^+\) ions were integrated into the organic and error matrices for PMF analysis. In this study, the PMF with 1 to 10 factors and Fpeak was varied from -1 to 1. After a detailed evaluation of mass spectral profiles, time series and comparison to the results of formerly reported mass spectra and supporting measurement data from other instruments, a five-factor solution at Fpeak=0 was chosen.

A time-of-flight chemical ionization mass spectrometer (ToF-CIMS) was used to measure concentrations of sulfuric acid (SA, H\(_2\)SO\(_4\)) and extremely low volatility organic compounds (ELVOCs)
(Junninen et al., 2010). The gas VOCs were monitored by a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) (Ionicon Analytik GmbH, Jordan et al., 2009). The heights of planetary boundary layer (PBL) at the measurement site were provided by HYSPLIT (Draxler and Rolph, 2013). The modelled PBL data was validated against the measurements by a Radiosonde. The aerosol number concentration and size distributions in a size range of 3-1000 nm were measured by a Differential Mobility Particle Sizer (DMPS). Other supporting measurement includes O₃, SO₂, CO, NOₓ, and meteorological parameters (wind speed, wind direction, precipitation, temperature, solar radiation and relative humidity) that are recorded continuously at the site throughout the year, details of which are described by Junninen et al. (2009).

RESULTS

Totally, five new particle formation events were selected (Table 1). All the events lie in the first half campaign time in the Finish Spring time when the nucleation event frequently takes place. For each event, the time covers the successive periods before and after nucleation moments for the purpose of exhibition of an overall picture of evolution of chemical composition throughout the new particle formation event. On average, the aerosol mass concentration during the five events was 1.0 μg m⁻³, which was one-third of the average value of the whole campaign. Concerning the chemical composition, organic component accounted for 58.5 %, sulfate 24.0 %, ammonium 7.3 %, nitrate 3.1 %, black carbon 6.3 % and chloride < 1 % of the total PM1 mass, respectively.

Table 1 The number sequence, time period, the mass concentrations of aerosol species during the new particle formation events that the study focuses on.

<table>
<thead>
<tr>
<th>Nucleation Number</th>
<th>Start</th>
<th>End</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0804</td>
<td>01:01 08/04/2014</td>
<td>08:40 09/04/2014</td>
</tr>
<tr>
<td>E1504</td>
<td>11:35 15/04/2014</td>
<td>09:03 16/04/2014</td>
</tr>
<tr>
<td>E2304</td>
<td>05:40 23/04/2014</td>
<td>08:52 24/04/2014</td>
</tr>
<tr>
<td>E2904</td>
<td>04:04 29/04/2014</td>
<td>08:29 30/04/2014</td>
</tr>
<tr>
<td>E0305</td>
<td>06:24 03/05/2014</td>
<td>13:49 04/05/2014</td>
</tr>
</tbody>
</table>

The size distributions, time series of aerosol components, and meteorological parameters during nucleation events in this campaign are shown in Figure 1. Firstly, we have systematically observed decrease of organic and sulfate aerosols in the measured mass concentrations. Secondly, we also observed a faster decrease rate of organic mass concentration than sulfate before the nucleation events (light pink bars, Panel D, Fig. 1). As a result, the mass fraction of sulfate to total aerosol mass increased, in contrast to a distinct decrease of organic fraction (light pink bars, Panel E, Fig. 1). The rapid decrease of aerosol concentrations was coinciding with the rising of PBL height when the sunrise starts in morning hours (refer to Fig. 2). The wind speed and wind direction were relatively constant before nucleation. Hence, the observed decrease of aerosol mass is firstly interpreted by a dilution effect on the aerosol concentrations due to the vertical air mass exchange with the development of PBL height. As a closer view, the development of PBL height coincided with the decreased aerosol mass as the UV radiation intensity strengthens. The height of boundary layer was then converted to dilution factors as a function of time. The time series of measured organic and sulfate mass concentrations and theoretical ones were shown in Fig. 2. The theoretical mass concentrations were calculated upon an assumption that the change of aerosol concentrations was controlled only by PBL height (multiplied by dilution factors). We have seen that the patterns of theoretical values were following the measured ones for both organic and sulfate species:
during the night, the aerosol particles were concentrated in the shallow boundary layer. In next morning when the PBL grows, air from free troposphere with a lower background aerosol concentration is entrained and mixed with the old aerosol population in PBL, leading to a decrease in the measured aerosol mass. However, the modelled aerosol concentrations were much smaller for sulfate and organic than the measured ones, suggesting the above mentioned dilution theory leads to an over-interpretation to the measurement data and other mechanisms also affected those two aerosol species.

![Graph 1](image1.png)

**Figure 1.** Observation of new particle formation events in E0305 during the campaign. Panel A: aerosol number size distributions from DMPS; Panel B: volume size distributions; Panel C: aerosol total number concentration; Panel D: mass concentrations of organic (green) and sulfate (red) species by AMS; Panel E: mass fraction of organic and sulfate to total aerosol mass concentration; Panel F: mass fraction of LVOOA and SVOOA to total organic mass concentration; Panel G: O:C ratio of organic species by AMS; Panel E: wind speed and direction.

![Graph 2](image2.png)

**Figure 2.** Dilution effect of PBL height on mass concentrations of sulfate (left panels) and organic (right panels) before nucleation events. Red/green diamond markers: sulfate/organic concentrations from the measurements. Solid lines: the modelled aerosol concentrations assuming PLB height to be an only
controlling factor on aerosol mass concentrations. The concentrations were calculated by accounting for the changes of air mass volume with PBL height. Dark diamond markers: the modelled aerosol concentration while also taking into account the condensation sink of sulfuric acid or ELVOCs in the gas phase.

CONCLUSIONS

The work presents the results of atmospheric aerosol evolution in response to the variation of planetary boundary layer height before and during nucleation events by using AMS. Even considering the efficient measurement of particle size range in the accumulation mode by AMS, we still observed the relative change of chemical composition of aerosol particles when the atmospheric nucleation events start. In the beginning of PBL growth, aerosol entrainment from the free troposphere controlled the observed aerosol composition and, in the later, the condensation of ELVOCs on the particles dominates the organic mass over the aerosol entrainment, whilst the aerosol entrainment still dominated the sulfate species. Our finding suggests that the mass concentrations of organic and sulfate aerosols before the nucleation events were the results of dynamics of the PBL development, atmospheric gas chemistry and aerosol entrainment.

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REFERENCES


METHOD FOR IDENTIFYING NEW PARTICLE FORMATION TYPES USING CHARACTERISTIC NUCLEATION-MODE PARTICLES AND AIR IONS

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INTRODUCTION

Atmospheric new particle formation (NPF) is a phenomenon which occurs around the globe (Kulmala et al., 2004; Kulmala et al., 2012, and references therein). It is defined as the secondary gas-to-particle formation of stable clusters with diameters below 2 nm and followed by their further growth, eventually reaching sizes capable of acting as cloud condensation nuclei (CCN). Besides their direct effect on human health and the environment (Harrison and Yin, 2000), the particles formed by NPF indirectly affect modifying many cloud properties relevant to climate (IPCC, 2013). Accordingly, scientists have performed extensive research and experiments to understand the NPF processes, as well as to characterize the parameters enhancing and inhibiting the formation of these particles (Nieminen et al., 2014 ;Ehn et al., 2014; Kirkby et al., 2016 ;Dada et al., 2016). Since NPF acts as a major source of aerosols and CCN (Merikanto et al., 2009; Kerminen et al., 2012), researchers have aimed to study long term available data sets to formulate a broad, clear picture on the mechanisms behind this phenomenon.

In order to determine whether a burst of particles can be classified as a NPF event, we followed the method proposed by Dal Maso et al. (2005). It classifies the days into three main categories based on the appearance of a new persisting mode of particles within diameter range from 3 to 25 nm. The classes defined are event days, during which such a mode appears, as well as non-events days and undefined days. Sub-classes of event days are also defined depending on the analyzability of the event. However, with improved instrumentation, e.g. NAIS (Neutral and Air Ions Spectrometer, Manninen et al. 2009), we are now able to detect particles < 3 nm in diameter, representing the initial steps of NPF. Here, we modified the classification of NPF events by applying the information whether the measurement site was within the NPF area (< 3 nm particles are detected), or whether the air masses from the NPF area had been transported to the site (only 3-25 nm particles are detected). Additionally, we determined the exact start-time and end-time for those events that were observed in the < 3 nm size range. This method allows, for the first time, to form a time series that defines an active time window for NPF, enabling us to study the properties and variables involved in NPF. We applied our method for a dataset of 11 years of continuous aerosol observations recorded at the SMEARII station in Hyytiälä, a boreal forest site located in southern Finland defined by low pollution and thus acts as a background semi-clean location. Those characteristics make Hyytiälä a representative location for NPF analysis by which the methods used here can be applied to other locations.

METHODS

The data in this study were collected at the Station for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR II) station, located in the boreal forest site in Hyytiälä, Southern Finland (61°51’N, 24°17’E, 181 a.s.l), Hari and Kulmala, 2005). The surroundings consist of mainly 50-year-old pine tree forests far from main pollution sources (Hari and Kulmala, 2005). Mobility distributions of charged and neutral aerosol particles and clusters in the size range of 0.8–47 nm have been measured at this site using a Neutral cluster and Air Ion Spectrometer.
Our event classification began by looking at two size classes of detected ion and particle concentrations for a given day, each used for different purposes: intermediate ions (2.25-4 nm) to confirm the initial cluster formation, and larger neutral particles (7-25 nm) to confirm the subsequent growth. The data were classified depending on the variations in ion and particle number concentrations in these two size ranges. Since we were only interested in daytime NPF, our method was set to detect NPF between 06:00 and 18:00. First, for cluster formation i.e. for ions (2.25 – 4 nm), a threshold value was taken from the mean ion number concentration during the previous night. The method then searched for consecutive number concentration of a constant values above this threshold forming a constant peak. If a peak of consecutive number concentration points was present, the start-time was set at the first crossing of the threshold line, the peak time was at the time when the maximum concentration was reached, and the end-time was the first crossing of the threshold line after the peak. Similarly, to confirm the growth of the freshly formed particles, the large particles (7-25nm) number concentration was investigated by finding a similar threshold and analysing whether it was exceeded within the hours following the event observed in intermediate ion concentrations.

RESULTS AND DISCUSSION

Days in Hytiälä were classified into five different classes. While less than 5% of the data points were unclassified due to missing NAIS data, the remaining four classes were separated based on whether either of the concentrations of intermediate ions or large particles reached the assigned peak value, or both. The classification is shown in Table 1. The ‘X’ mark in each box means that the number particle concentration reached the assigned peak value.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Intermediate ions (2.25-4nm)</th>
<th>Large particles (7-25nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Events in Hytiälä</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Transported Events</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Ion Burst</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Non-event</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NPF events in Hytiälä were defined by the appearance of a concentration of intermediate ions that exceeded the threshold value, which after a delay is followed by an appearance of large particles. The non-events on the other hand, are defined by absence of intermediate ions as well as neutral larger particles. When only one of the marker concentrations (intermediate ions or Large particles) is present, the day is classified as: i) ion burst, in case the intermediate ions appeared, but yet they do not grow further to form larger neutral particles; ii) transported event in the case when no intermediate ions are present (those that represent initial steps of NPF), yet larger particles are present. The latter class results when a NPF event occurs nearby and the air mass is then transported to the measurement station. Our results (Events in Hytiälä + Transported Event frequency) fell in agreement up to 88% (Events) with the old classification method proposed by Dal Maso et al. 2005. Using the 11 years of available data from NAIS, our results show the fraction of days included in each class (Figure 1). Also, we were able to extract the trends of frequency of NPF type in different years, as well as in different seasons. We found that events occurring in Hytiälä are more frequent in the spring while the transported ones events are most frequent in summer.
CONCLUSIONS

Using concentrations of nucleation mode air ions and particles we are able to identify different types of NPF events in Hyytiälä, southern Finland. Our method relies on data collected using a NAIS between the years 2006 and 2016. The new classification divides the studied days into five different types: events in Hyytiälä, transported events, ion bursts, non-events and unclassified days. Besides minimizing the number of undefined days from 50% in the old classification to less than 5% in the current one, our method enables identifying the start-times and end-times of events occurring in Hyytiälä, and thereby forming a time series which points out the active time window of NPF. This will help us to understand the meteorology and variables that determine whether or not a NPF event occurs. Our results serve best to characterize NPF in other locations and specify the exact type of events. Our aims are also linked to understand the variables that play a role in defining NPF types.

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REFERENCES


Integrated evaluation of biogenic secondary organic aerosol formation in a global climate-model

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INTRODUCTION

Atmospheric formation of nanometer sized particles through gas to particle conversion processes is a frequent phenomenon which significantly contributes to global aerosol particle number concentration throughout the troposphere (Merikanto et al., 2009). Besides their effect on human health, these particles can, after they grow to larger sizes, act as cloud condensation nuclei (CCN), and impact climate through cloud related radiative processes (e.g. Kerminen et al., 2012). Global models predict that new particle formation (NPF) could produce a substantial fraction of the total CCN budget, up to 70% in some regions (Merikanto et al., 2009; Yu and Luo, 2009), and in turn strongly control the present-day climate forcing by aerosol particles.

Despite the fact that instrumentation is continuously being improved, our understanding of the aerosol formation mechanism still remains incomplete. For that reason, global models use simplistic representations of the process which are assumed to cover a large range of atmospheric conditions. Efforts have been put during the last decades to better constrain predictions to observations in the planetary boundary layer (e.g. Makkonen et al., 2009), where first attempts to describe nucleation were originally done using the binary nucleation mechanism derived from the classical nucleation theory (Spracklen et al., 2005). Parameterizations have evolved towards a more explicit description of the involvement of oxidized organic compounds from biogenic origin in the very beginning of the NPF process (e.g. Paasonen et al., 2010), as widely suggested by recent observations.

However, when evaluated against observation, the predictions of NPF and its related effects have often been discussed with respect to the choice of the parameterization for the nucleation step, while the discrepancies related to the accuracy of the predicted precursors concentrations themselves were most likely left behind further investigation. Here we report such an analysis for commonly used precursors in models, i.e. monoterpenes and their oxidation products, hereafter referred as HOMs (Highly Oxidized Multifunctional organic compounds), as well as sulfuric acid, using simulations conducted with the global model ECHAM5.5-HAM2 (Stier et al., 2005; Zhang et al., 2012) and measurements performed at the boreal SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005).

METHODS

Monoterpenes volume mixing ratios (VMRs) were measured in Hyytiälä with a quadrupole Proton Transfer Reaction Mass Spectrometry (PTR-MS), which allows real-time monitoring of VMRs down to tens of ppt. Monoterpenes concentrations were derived from the signal obtained at m/z (mass-to-charge-ratio) 137 (Taipale et al., 2008). Sampling was performed close to the top of the forest canopy, i.e. 14 or 16.8 m, every second or third hour. In order to filter out extremely high monoterpenes concentrations related to the activity of the nearby sawmill, we applied the modified Thompson tau method, as previously suggested by Liao et al. (2011).

Because of the lack of continuous measurement during the whole period of interest, HOMs and sulfuric acid concentration were derived from proxies (Kontkanen et al., 2016; Petäjä et al., 2009). However, measurements performed with a nitrate ion based chemical ionization Atmospheric Pressure interface Time-Of-Flight (CI-API-
TOF) mass spectrometer (Jokinen et al., 2012) on shorter periods were used in addition. The calibration of the instrument was based on sulfuric acid detection, and the resulting calibration coefficient was assumed to allow also for the determination of HOMs concentration. Measurement uncertainty is estimated to be in the range -50%+/100%, because of both calibration and transmission related effects.

More information regarding the oxidation capacity of the atmosphere with respect to monoterpenes was obtained from measurements and/or estimations of the main oxidant concentrations, i.e. OH, O3 and NOx. O3 concentration was directly measured with an ozone analyser based on the absorption of UV radiation. In contrast, OH and NOx concentrations were calculated from measurements of other parameters, including NO and NOx concentrations (chemiluminescence analyser) as well as UVB-radiation (SL 501A pyranometer) and temperature (PT-100 sensor), all performed at 16.8 m except for radiation (18 m). Finally, the identification of NPF event days as well as the calculation of early particle growth was performed using measurements conducted with AFS (Air Ion Spectrometer; Mirme et al., 2007) and BSMA (Balance Scanning Mobility Analyser; Tammet, 2006). Additional particle concentrations were measured using a DMPS (Differential Mobility Particle Sizer).

The ECHAM5.5-HAM2 model was run over the period of 2000-2010 using nudging technique to assimilate model meteorology towards ERA-Interim. The emissions of dust and sea salt were calculated online, while anthropogenic emissions of OC, BC and SO2 were taken from ACCMIP emission inventory. The model has been upgraded with a secondary organic aerosol (SOA) scheme including ELVOCs (Jokinen et al., 2015), and ELVOCs are participating in the nucleation of new particles (Paasonen et al., 2010). The emissions of BVOC emissions were either taken from pre-calculated fields from MACC inventory, or calculated online using MEGAN algorithm. Here we show results from prescribed BVOC emission simulations.

Direct comparison of modelled and measured values was achieved for monoterpenes concentrations, oxidants concentrations, particle growth rates as well as particle concentrations. In contrast, indirect comparison was performed for HOMs and sulfuric acid, which concentrations are not explicitly traced in the model. Instead, their contribution to early particle growth, directly retrieved by the model and deduced from measured or proxy-derived concentrations in Hyytiälä, was investigated as an indicator.

CONCLUSIONS

This analysis, based on a long-term dataset, allowed us to investigate how the accuracy of predicted precursors concentrations might, besides the choice of the parameterization itself, affect prediction of NPF and its effects, including especially particle concentrations in different diameter ranges up to CCN relevant sizes. As shown on Figure 1, similar seasonal trends were observed for modelled and measured monoterpenes concentrations over the 2007-2010 period. Best agreement was obtained between April and November, suggesting that winter time predictions could be more especially affected by missing processes in the model. Regarding particle growth rates in the 1.5-3 nm size range, comparison conducted over an extended period (2003-2010) revealed contrasting seasonal variations (Figure 2), most likely related to the fraction of growth ascribed to sulfuric acid. Several reasons are suggested to explain the aforementioned discrepancies, including the strength of precursors emissions in the model, the calculation of their sinks as well as the treatment of oxidation processes.

While participating in the identification of factors causing uncertainties in the prediction of NPF and its related effects, this work will help better constraining the process in global models.
ACKNOWLEDGEMENTS

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REFERENCES


TEMPERATURE DEPENDENCE OF PARTICLE NUMBER CONCENTRATION PRODUCED BY A TWO STROKE ENGINE

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Keywords: particle nucleation in combustion, semi-volatile organics.

INTRODUCTION

Vehicle emissions are one of the most significant contributors to pollution in urban areas and they constitute a specially harmful type of pollutant due to the exposure of population exposed to it. Aerosol particles produced by internal engine combustion are a complex mixture of organic carbon and elemental carbon, sulfate, and many other chemical species. Depending on the specifics of the measurement technique utilized, i.e., temperature, dilution particles can nucleate, or change phase during the process. Internal combustion engines are also strong contributors to particle number concentration emissions. Freshly nucleated particles from engine exhaust are a substantial source of Secondary Organic Aerosol precursors. However, accurate measurement of these particles is challenging, and transformation of the particle size distribution of particles in the sampling system is a concern that must be accounted for.

In this work, we assess the problem of accounting for emergence of a nucleation mode in measurements of exhaust emissions. The problem is approached through a combination of experimental and modeling techniques to understand the impact that freshly nucleated particles have on the size distribution of exhaust emissions from a two stroke engine. A new data inversion method for the DMM-230 instrument is presented.

METHODS

Measurements where performed with an electric low pressure impactor, DMM-230, Dekati ltd., 2007, (Lehmann et al., 2004; Mamakos et al., 2006; Mariq et al., 2006). This instrument has a corona charger, a electrical mobility analyzer, and a cascade impactor with six impaction stages. The particle detection in the instrument is performed through the measurement of the current generated by the impacted particles in the impaction stages. The aerodynamic cut diameters for the impactor stages go from 30nm to around 1.2µm. The smallest particles are detected in a mobility stage, where particles smaller than 30nm pass through a simple mobility analyzer.

In order to analyze the collected data set, a sectional aerosol model is employed to simulate the transformations undergone by the aerosol size distribution from the engine exhaust, through the dilution system, up to the DMM-230. The Two-Moment Aerosol Sectional (TOMAS) model of Adams and Seinfeld (2002) is used. The two moments are the aerosol number density, Nk, and the mass density, Mk, where k is the bin number. The number and mass distributions are discretized into 30 bins, defined by mass doubling. which number concentration, and mass of sulfate, organics, black carbon, and water are tracked. The TOMAS model in our study is setup following (Singh et
al., 2014), which includes nucleation (Vehkamaki and Lehtinen, 2003), Brownian coagulation, and condensation/evaporation of two organic species. Aerosol particles are assumed to be formed of five components, elemental carbon (EC), water (H$_2$O), sulphate (SO$_4$), and two components of semi-volatile organic carbon (OC). Water in the particle phase is calculated by assuming equilibrium with relative humidity in the gas phase. The two-component organic carbon model used here was used successfully to predict partitioning in other studies (Shrivasrava et al., 2006). The model is used in this work to predict condensation/evaporation of OC onto existing particles. Component 1 has molecular weight of 282 g/mol and saturation concentration of 1784 µg/m$^3$, while component 2 has a molecular weight of 394 g/mol and saturation concentration of 8 µg/m$^3$. The total organic is distributed 58% to component 1 and 42% to component 2.

Finally, a new data inversion method is developed for the raw data of the DMM-230. This method allows to calculate the number size distribution without the need of assuming a log-normal shape for the size distribution. The data inversion method is based on the work of (Mamakos et al., 2007). In this way, the presence of nucleated particles is detected in the mobility channel (≤ 30nm). This detailed post processing system for the raw data is performed to infer the number size distribution of the particles detected by the DMM-230. The methodology was then tested on the emissions generated by a small, two-stroke engine. The engine has a displacement of 50cc.

**CONCLUSIONS**

The measurements performed in this study show extremely high emission rates of sub-micrometer particles, both, in mass and number concentration, by the small two-stroke engine.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Measured Concentration (µg/m$^3$)</th>
<th>Emission Factor (gPM/kg$_{fuel}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Idle</td>
<td>$6.7 \times 10^4$</td>
<td>121.5</td>
</tr>
<tr>
<td>Full Throttle</td>
<td>$3.0 \times 10^5$</td>
<td>266.1</td>
</tr>
<tr>
<td>Drive Cycle</td>
<td>$4.5 \times 10^5$</td>
<td>184.9</td>
</tr>
</tbody>
</table>

Table 1: Average fuel-based mass emissions observed during experimental phase.

Aerosol size distribution simulations with the TOMAS model, suggest that careful analysis of the data and the temperature profile inside the experimental setup needs to be considered when measurements are performed with heated dilution air.

Our measurements and modeling approach reveal a extreme sensitivity of the system, to both, dilution ratio, and temperature of dilution air. When dilution air is injected into the system, there is a clear increase in the current of the mobility channel, while the current in the remaining six channels decreases considerably. This situation implies the clear emergence of nucleation mode particles. Despite the dilution might sharply decrease gas phase organics concentration, the sudden temperature increase can volatilize material from the particle phase. Any decrease in the temperature in the sampling system can result in a return of the less volatile components to the particle phase.

**ACKNOWLEDGEMENTS**

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REFERENCES


NEW PARTICLE FORMATION AT RURAL BACKGROUND SITE IN WESTERN SAUDI ARABIA


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Keywords: aerosol particles, new particle formation, number concentration, size distribution

INTRODUCTION

The Arabian Peninsula is one of the strongest aerosol particle source areas, both natural and anthropogenic, in the world. As a part of so-called dust belts, natural aerosol mass is dominated by desert dust, which can be transported over large distances (Prospero et al., 2002). Dust storms and episodes strongly change aerosol physical and optical properties causing strong perturbation into radiation-energy balance and air quality (e.g. Alam et al., 2014). Anthropogenic emissions mainly originate from road traffic, petroleum industry and local constructions (Khodeir et al., 2012). The size distributions, optical properties, and physico-chemical properties of aerosol particles are highly variable in such regions. In this study the physical properties of aerosols are, for the first time, comprehensively derived at a rural background area in Saudi Arabia. The study concentrates on aerosol number size distribution measurements, which reveal that atmospheric new particle formation events take place frequently in the region and that these events often show a shrinking mode mean diameter towards the end of the observed event.

METHODS

The Hada Al Sham site (21.802° North, 39.729° East, 254 m a.s.l.) is situated about 60 km east of the coastal city of Jeddah. The surroundings represent a rural area. The following in situ measurements are conducted at the station: PM$_{2.5}$ and PM$_{10}$ mass concentrations, total particle number concentration, particle number size distribution from 7 nm to 10 µm, aerosol black carbon concentration (absorption coefficient) and aerosol scattering coefficient. Cimel sunphotometer is used for measuring the columnar properties of the atmosphere. In addition, weather parameters are measured. More detailed description can be found from Lihavainen et al. (2016).

We analyzed aerosol size distribution data measured with a twin Differential Mobility Particler Sizer (DMPS) measuring from 7 nm to 850 nm in particle diameter over the measurement period from February 2013 to February 2015. The data coverage was around 64 %. New particle formation (NPF) event classification was done for the measurement days following the methods described by Dal Maso et al. (2005). NPF events were further separated into subclasses depending on whether they showed a clear shrinking mode during the later stages of the event or not. The next step in the analysis is to determine the
particle growth rates for the NPF event days, and calculate the formation rates of particles with diameter of 6 nm (the smallest diameter detected with the DMPS) as described by Kulmala et al. (2013). Additionally, we will inspect more carefully those NPF event days on which the mode mean diameter is observed to decrease with time (as seen in Figure 1, roughly between 96.7 and 96.8). The occurrence of the shrinking mode mean diameter will be compared with the meteorological parameters, in order to discover the reason for this phenomenon. The shrinkage of newly formed aerosol particles has been earlier observed in other environments, but so far not explained (Yao et al., 2010; Young et al, 2013; Salma et al., 2016).

RESULTS

The average total number concentration was around 10630 ± 9880 cm³ and daily maximum 23100 cm³. The one hour averages varied between 630 and 99300 cm³. The total number concentration was dominated by new particle formation and growth events, which were observed on over 70% of all valid days. An example of a typical new particle formation event is presented in Figure 1. Total number concentrations started to increase when the Sun rose and the sea breeze started, bringing to the station the air masses from the direction of Jeddah. This is the time when new particle formation started. During the day, the formed particles grew to larger sizes. The growth was very fast, and particles from new particle formation and growth were able to influence aerosol optical properties. Quite a typical feature of the new particle formation events was that the growth of the particles stopped or even turned into shrinking during the afternoon, when the wind direction started to turn from west towards east.

![Image](image_url)

Figure 1. New particle formation event and subsequent growth as seen on April 2014 in Hada Al Sham. Horizontal axis is the day of year, on the top vertical axis is particle diameter and color presents concentration. In the bottom figure the vertical axis is the total number concentration.
The results of the NPF event classification are shown in Figure 2. NPF events were observed very frequently (on 73% of the days). The amount of days that clearly showed no formation of new particles was almost nonexistent, especially, since many of the days classified as undefined showed bursts of new particles, but the features of these bursts were too unclear to be defined as NPF events. In the majority of the events, the growth of new particles was followed by a shrinking mean diameter mode. The results of the analysis on particle growth and formation rates will be presented at the conference.

Figure 2. Breakdown of the NPF event classification. The total number of classified days was 455.

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REFERENCES


THE EFFECT OF BISULFATE, AMMONIA, AND AMMONIUM ON THE CLUSTERING OF ORGANIC ACIDS AND SULFURIC ACID

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Keywords: ION-INDUCED NUCLEATION, MOLECULAR CLUSTERS, QUANTUM CHEMISTRY

INTRODUCTION

According to current knowledge, new-particle formation is believed to involve sulfuric acid coupled with a stabilizing component such as ions, bases, or oxidized organic compounds. We have previously studied the cluster formation between sulfuric acid and pinic acid or MBTCA and found a favorable interaction between the organic acids and sulfuric acid (Elm et al. 2014). However, using cluster kinetics calculations we showed that the growth of the clusters are essentially limited by a weak formation of the largest MBTCA-sulfuric acid clusters, suggesting that pinic acid and MBTCA cannot contribute the cluster growth when clustering occurs via neutral pathways (Elm et al. 2017). Here we have investigated the stabilizing effect of the bisulfate anion, ammonium cation, and ammonia on the ability to enhance cluster formation between sulfuric acid and pinic acid or MBTCA. Figure 1 shows the pinic acid (C₉H₁₄O₄) and MBTCA (C₈H₁₂O₆) monomer molecular structures.

![Figure 1. The molecular cluster structure of pinic acid (left) and MBTCA (right).](image)

METHODS

Cluster structures have sampled using semi-empirically guided technique, which should yield a good guess for the global minimum. For the lowest energy structures, geometries are optimized and frequencies are calculated using the three density functionals M06-2X, PW91, and oB97X-D with the 6-31++G** basis set. Electronic energy corrections were performed using DLPNO-CCSD(T)/def2-QZVPP level of theory on top of the DFT structures. This multi-step quantum chemical approach has been shown to yield reliable Gibbs free energies (Myllys et al. 2016). The stability of the clusters is evaluated based on the calculated formation free energies.
CONCLUSIONS

The presence of ammonia, bisulfate, or ammonium is found to enhance the interaction between organic acids and sulfuric acid. Figure 2 shows the molecular structure of \((\text{MBTCA})_2(\text{H}_2\text{SO}_4)_4(\text{NH}_4^+)\) cluster. Ammonium ion is in the core of the cluster and it forms hydrogen bonds with organic acid and sulfuric acid, which stabilize the cluster structure.

![Figure 2. The molecular structure of \((\text{MBTCA})_2(\text{H}_2\text{SO}_4)_4(\text{NH}_4^+)\) cluster.](image)

Figure 3 shows the Gibbs free energy diagram for pinic acid clusters. The clusters containing bisulfate, ammonia, or ammonium are more likely to growth than solely pinic acid-sulfuric acid clusters. The interaction between organic acids and sulfuric acid are found to be thermodynamically more favourable when cluster contains some stabilizing compound (Myllys et al. 2017). Especially the presence of bisulfate or ammonium ion makes the cluster formation more favourable.
Figure 3. Gibbs free reaction energy diagram for pinic acid clusters at 298 K and 1 atm calculated at the DLPNO-CCSD(T)/def2-QZVP//DFT/6-31++G(d,p) level of theory. Red > -5 kcal/mol, yellow -5 -- -10 kcal/mol, and green < -10 kcal/mol. P=pinic acid, A=sulfuric acid, B=bisulfate, N=ammonia, and C=ammonium.

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REFERENCES


OBSERVED DIFFERENCES BETWEEN EVENT AND NON-EVENT DAYS IN LEVELS OF AMINE AND AMMONIA CONTAINING COMPOUNDS

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Keywords: New Particle Formation, Dimethylamine, Sulfuric Acid, Organics.

INTRODUCTION

Atmospheric aerosol particles are known to affect both the climate (IPCC, 2013) and human health (Harrison and Yin, 2000). Thus comprehending the sources of these particles is important. One of the important sources for atmospheric aerosols, particularly regarding particle number concentrations, is new particle formation (NPF). It has been observed to take place all over the world in various atmospheric conditions (Kulmala et al., 2004). The importance of sulphuric acid and highly oxidized organics in NPF has been shown in several studies, both in laboratory studies (Sipilä et al., 2010) and field measurements (Petäjä et al., 2011; Kulmala et al., 2013). However, other components may also affect NPF and the observed nucleation rates. Ammonia and amines have been suggested to act as stabilizing agents in new particle formation events (Kürten et al., 2014; Lehtipalo et al., 2016) and they can also participate in the growth of atmospheric aerosol particles (Bzdek et al., 2010). Here we studied the measured concentrations of dimethylamine, ammonia, sulphuric acid and calculated oxidized organics concentration and their behaviour during NPF events.

METHODS

The data used in this study were obtained at the SMEAR (Station for Measurement of Ecosystem-Atmosphere Relations) II station (Hari and Kulmala, 2005) during January 2013 - December 2015. The station provides continuous comprehensive measurements of quantities describing the forest-atmosphere interactions. The station is located in Hyytiälä, Finland (61°51′0″N, 24°17′0″E), about 220 km north of Helsinki. Hyytiälä is considered a rural background site because of low levels of pollutants due to its distance from any major cities.

Aerosol size distributions from a differential mobility particle sizer (DMPS) measurements were used for classifying individual days as either NPF event or non-event days (Dal Maso et al., 2005). Undefined days were excluded from our analysis. Because NPF events are typically observed around noon we used the median values from 9:00 in the morning to 12:00 noon in our analysis. All compounds used in the analysis were also normalized with their respective medians over the length of the data set in order to compare the relative changes of the concentrations.

In this study we used measured gas phase sulphuric acid (SA, H₂SO₄), dimethylamine (DMA, (CH₃)₂NH) and ammonia (NH₃) concentrations and a modelled proxy calculations for oxidized organics concentration (OxOrg) (Kontkanen et al., 2016). Sulphuric acid was measured using a chemical ionization atmospheric pressure interface mass spectrometer (CI-API-TOF) with nitrate ion as the charger ion (Jokinen et al., 2012). Ammonia concentrations utilized in this study
were measured using a semi-continuous ion-chromatograph MARGA (Applikon, Breda Netherlands). In the instrument gases were trapped in water solution in a wet rotating denuder and aerosols in a steam jet aerosol collector. Hourly injected samples were analysed using an ion chromatograph equipped with conductivity detectors (LiBr used as an internal standard). For amine measurements an electrospray ionization quadrupole MS-detector (Shimadzu LCMS-2020, Kyoto Japan) was connected to the MARGA. With this system seven different amines (monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA), propylamine (PA) and butylamine (BA)) were measured using deuterated diethyl-amine (Isotec TM; Sigma-Aldrich, St. Louis, USA) as an internal standard. Calibration with external calibration solution was run every two weeks for all the measured amines. Instrumental blank values, measured roughly every month, were subtracted from the results. Data coverage of 56 and 108 days were recorded for DMA and ammonia, respectively, in comparison to sulphuric acid data, which had a total of 635 days of available data. Days with missing data were excluded from our analysis.

The estimated NPF rate can be calculated by multiplying the concentrations of the vapours required to form the smallest cluster, which can be taken as an efficiently growing particle (McMurry and Friedlander, 1979; Kulmala et al., 2006; Metzger et al., 2010; Paasonen et al., 2010). Here, we study the homogenic heteromolecular nucleation mechanism and test several combinations of vapours for it. We compared whether there is a clear separation between NPF event and non-event days in values of NPF rate calculated as

$$J = K_{het}[X]^a[Y]^b[Z]^c,$$

where X, Y and Z are different vapours and a, b and c are integers, related to the number of molecules of each vapour required in a cluster for new particle formation.

We systematically tested several combinations of sulphuric acid, oxidized organics, dimethylamine and ammonia to determine if any clear separation is present between NPF event days and non-event days. Several different powers for the compounds were tested.

RESULTS

The main results of our work are summarized in Figure 1 showing some combinations tested in the study. The clearest separation was achieved with a combination of sulphuric acid, oxidized organics and dimethylamine as $[\text{H}_2\text{SO}_4][\text{OxOrg}]^3[\text{DMA}]$, suggesting that these molecules are crucial in NPF. Switching dimethylamine with ammonia still provides a visible separation, but not as notable as with DMA. These results suggest that sulphuric acid and oxidized organics alone are not enough to explain event days at our measurement site.

CONCLUSIONS

The results presented in this study show that including dimethylamines or ammonia with SA and OxOg significantly increases the separation between event days and non-event days, thus pointing at the importance of these gases in new particle formation events. This indicates that new particle formation also requires base components to occur and that in the boreal forest environment, the main pathway for NPF would involve sulphuric acid, oxidized organics and dimethylamine. However, these results are based on a small data set out of which it is difficult to make conclusive remarks. In addition, DMA measurements have large uncertainties, as shown by the drastically different results on DMA presented by Sipilä et al. (2015) and Kielloaho et al. (2013). A larger dataset and more research is required to provide more conclusive evidence. If possible, these
Figure 1: Median values of vapour concentrations and different combinations of them for NPF event and non-event days. The box contains all data within the 25th and 75th percentiles, and the red line is the median. The whiskers include all data points that are at most 1.5 times the interquartile range away from the median. Data outside the whiskers are considered outliers and are marked with red crosses.

measurements should also be conducted in other locations than SMEAR II to determine their viability for other atmospheric conditions as well.

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REFERENCES


OBSERVATIONS OF A DIURNAL CYCLE OF ICE NUCLEATING PARTICLE CONCENTRATION ON THE SHOULDERS OF MT. KENYA

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Keywords: ICE, NUCLEATION, MT. KENYA

The Mt. Kenya Global Atmospheric Watch station (0.062°S, 37.297°E, 3678 m a.s.l., Fig. 1) is a uniquely situated observational station for making atmospheric measurements. Its high-altitude location means that the ground level station is exposed to a strong diurnal cycling of descending free-tropospheric air at night and rising, mixed boundary layer air during the day. Additionally, because it is at the geographic equator the station is alternately situated within the northern and southern air masses as the inter-tropical convergence zone (ITCZ) progresses through its annual south to north migration, following the sun’s path of maximum irradiance. The station’s location and exposure to this atmospheric cycling make it uniquely suited to make temporally contiguous measurements of regional and hemispheric air masses.

During August and September 2015 a measurement campaign was undertaken to quantify the number concentration of ice nucleating particles (INP) present at the Mt. Kenya station. For ≈ 3 weeks, twice daily samples were collected by electrostatic precipitation of aerosol particles onto silicon substrates, the INP on the substrate were subsequently activated and analyzed in the

Figure 1: Location of the Mt. Kenya station (MKN), and the approximate minimum and maximum latitudinal extents of the ITCZ. The general flow over the western Indian Ocean, including the East African Low Level Jet (ELLAJ) are also indicated. Figure taken from (Henne et al., 2008).
isothermal static diffusion chamber FRIDGE (Schrod et al., 2016) at temperatures between -20°C and -30°C and relative humidity with respect to ice from 115 to 135%. Additional meteorological and gas and particle phase aerosol monitoring were undertaken to compliment the INP measurements. In order to characterize the diurnal air mass cycling with respect to INP both daytime and nighttime samples were taken at times when the air mass signal could be clearly confirmed by real-time, temperature, wind direction and aerosol particle concentration measurements.

Here we present results from the measurement campaign which illustrate the air mass cycling and the clear presence of a diurnal cycle of INP. The differences between the regional and hemispheric sources are mapped and discussed.

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REFERENCES


ICE NUCLEATION AND ANTIFREEZE PROPERTIES OF BIOLOGICAL MACROMOLECULES

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Keywords: ICE NUCLEATION, ICE GROWTH INHIBITION, POLLEN

INTRODUCTION

The formation of ice crystals via ice nucleation and growth is an important and widespread environmental phenomenon, for example during atmospheric ice cloud formation or in living organisms at subfreezing temperatures. Nature has developed means to either promote ice crystal formation, e.g. via ice-nucleating proteins, or inhibit ice crystal growth, e.g. by antifreeze proteins. Recent studies have pointed towards the atmospheric importance of biological particles in the nanometer-to-micrometer size range, including pollen, bacteria, microalgae, fungal spores and cellulose. For some of these particles the ice-nucleating active sites are macromolecules such as proteins or polysaccharides. Ice-nucleating molecules can also be released from the particles as dissolved hydrated molecules or suspended molecular clusters, as has recently been shown for pollen (Pummer et al., 2012). Here, we investigate biological macromolecules released from various types of pollen regarding their ice-nucleating ability as well as their antifreeze properties (Dreischmeier et al., 2017).

METHODS

The ice nucleation behavior of various molecular ice nucleators in inverse (water-in-oil) emulsions was investigated by differential scanning calorimetry (DSC). Homogeneous or heterogeneous ice nucleation (i.e., exothermic processes) and ice melting (endothermic) were measured as the difference in heat flow between the sample pan and an empty reference pan. Ice nucleation measurements were performed at a cooling rate of $-5 \, ^\circ C \, min^{-1}$ and ice melting investigations at a heating rate of $+1 \, ^\circ C \, min^{-1}$. Emulsions were prepared by mixing 2 mL of an organic phase, consisting of 7 wt% of the surfactant Span 65 dissolved in a 1:1 by volume mixture of methylcyclohexane and methylcyclopentane, and 2 mL of the aqueous phase of interest containing the ice nucleators. This mixture was stirred with a high-speed disperser at room temperature for 10 min at 20,000 rpm to generate an emulsion containing aqueous droplets about 1-10 µm in size. About 7 mg of an emulsion was transferred into a hermetically-sealed aluminium DSC pan for immediate measurement.

Alternative ice nucleation measurements were performed using an optical freezing array (BINARY: Bielefeld Ice Nucleation ARraY). Here, macroscopic (1 µL) droplets were deposited on a hydrophobic glass slide using a microliter pipette dispenser. Each droplet is enclosed and separated from the other droplets using a polydimethylsiloxane spacer. Droplet freezing at a cooling rate of $-1 \, ^\circ C \, min^{-1}$ was determined optically by means of a digital camera.

We also studied whether the biological macromolecules showed typical antifreeze properties such as ice shaping and ice recrystallization inhibition. The activity of molecules was analyzed in an
aqueous sucrose solution with a mass fraction of 0.3. A droplet of sample solution (about 5 µL) was embedded as a thin film between two glass coverslips sealed with silicone grease. This sample cell was then placed onto a temperature-controlled stage which is part of an optical microscope setup equipped with a digital camera. Rapid cooling to low temperatures (between −30 °C and −40 °C) resulted in polycrystalline ice, which was then slowly heated to just below the melting temperature leaving only a few remaining ice crystals. After only one or two ice crystals were left in the field of view, very slow cooling at a rate of −0.01 °C min⁻¹ was initiated, and the resulting very slow crystal growth was recorded with digital microphotographs taken every few seconds.

Finally, we investigated whether the biological molecules affected ice growth by studying the kinetics of ice recrystallization of polycrystalline ice samples. For this purpose we employed the Ice Recrystallization Rate INhibition Analysis (IRRINA) assay (Budke et al., 2014) for aqueous sucrose solutions (mass fraction 0.45) containing the biological macromolecules. A thin film is formed by pressing 2 µL of such a sample solution between two glass coverslips. This sample cell was then introduced into the temperature-controlled optical microscope setup as described above. Thereafter, the sample was cooled quickly to −50 °C, thereby producing a polycrystalline ice film. Subsequently, the sample was heated to −8 °C, where it was observed for 2 hours while microphotographs were taken every 15 s. The cubic mean radius of all those ice crystals within the field-of-view was obtained using image analysis, and its time dependence was analyzed using Lifshitz-Slyozov-Wagner theory.

RESULTS

One result of the experiments is that birch pollen release both ice-nucleating molecules as well as ice-binding molecules with antifreeze properties. For example, a stock solution of birch pollen macromolecules (Fig.1a, top panel) shows heterogeneous ice nucleation at about −18 °C in DSC experiments (Fig.1b, top panel) and also shaping of ice crystals into an hexagonal crystal habit (Fig.1c, top panel).

![Figure 1: Ice nucleation and ice shaping of aqueous solutions of birch pollen molecules before (stock solution) and after centrifugal filtration (supernatant and filtrate). Adapted with changes from Dreischmeier et al. (2017).](image)
In order to characterize the ice-active molecules in terms of their molecular size we employed centrifugal filtration. A stock solution of purified macromolecules was applied to a centrifugal filter with a 100 kDa molecular weight cut-off, such that molecules larger than \( \sim 100 \) kDa remain in the supernatant, and those smaller than \( \sim 100 \) kDa pass the filter into the filtrate (Fig.1a). Thereafter, the supernatant and filtrate were investigated to determine a potential size dependence of the ice nucleating and ice-binding activity. The supernatant shows heterogeneous ice nucleation nearly identical to that of the stock solution (Fig.1b, middle and top panel, respectively), while ice shaping is practically diminished (Fig.1c, middle panel). In contrast, the filtrate does not show ice nucleation activity (Fig.1b, bottom panel), but does exhibit ice shaping (Fig.1c, bottom panel). These observations suggest that molecules larger than \( \sim 100 \) kDa are responsible for ice nucleation, and molecules smaller than \( \sim 100 \) kDa do show ice-binding antifreeze properties. Interestingly, chemical analysis of the molecules by means of Fourier Transform Infrared spectroscopy in attenuated total reflection mode reveal that both types of molecules have very similar chemical structures: they are polysaccharides bearing carboxylic moieties. We have also investigated molecules of other types of pollen for the ice nucleation and antifreeze activity and compare their results with those of birch pollen macromolecules. For more details see Dreischmeier et al. (2017).

CONCLUSIONS

Birch pollen washing water exhibits heterogeneous ice nucleation activity, but also shows ice-binding properties such as ice shaping and ice recrystallization inhibition, similar to antifreeze proteins. Both types of functions are induced by very similar acidic polysaccharides released from the pollen upon suspension in water. However, centrifugal filtration indicates differences in molecular size: the ice-nucleating molecules are larger than \( \sim 100 \) kDa, while ice shaping is due to smaller molecules. These results may suggest that the larger ice-nucleating polysaccharides consist of clusters of the smaller ice-binding polysaccharides, or that the latter are fragments of the ice-nucleating polysaccharides.

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REFERENCES


AIRBORNE PM$_{2.5}$ CONCENTRATION IMPROVEMENT UNDER VARIOUS CONTROL SCENARIOS – A CASE STUDY IN TAIWAN

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Keywords: PRIMARY PM$_{2.5}$, SOx, NOx, CONTROL MEASURE, CMAQ

INTRODUCTION

Fine particulate matter (PM$_{2.5}$) issue has been a concern around the world and is also a hot environmental topic in Taiwan for decades. The annual average concentration of PM$_{2.5}$ around Taiwan is 20.0 $\mu$g/m$^3$ and with great variation in different regions (9.3 – 28.5$\mu$g/m$^3$). The Taiwan Environmental Protection Administration (TEPA) adapted the ambient air quality standard of PM$_{2.5}$ (annual average concentration as 15$\mu$g/m$^3$) and developed a control program to improve the ambient concentration by reducing the emissions of primary fine particulate matter and the precursors of secondary PM$_{2.5}$. However, the plan does not evaluate the improvement of airborne PM$_{2.5}$ concentration nor the further reduction requirement. This study investigated the potential improvement of ambient PM$_{2.5}$ concentration by the TEPA program and the other scenario for further emission reduction on various sources.

METHODS

Potential improvement of ambient PM$_{2.5}$ concentration was evaluated by air quality modelling work. Both primary fine particulate matter and secondary particulate matter were evaluated. The TEPA program has several measures, including adoption of more stringent emission standards for stationary sources and on-road mobile sources, eliminating the high-polluting aged vehicles, and promoting electric vehicles. Emissions of primary PM$_{2.5}$ and precursor gases (SOx, and NOx) before and after the implementation of TEPA program were calculated according to the measures in the program. The further reduction scenario was proposed to take more control measures on stationary sources and mobile sources. Three scenarios had been evaluated in this study. Basic scenario represents the case of business as usual without implementation of this program. Scenario A represents the potential improvement of air quality as the TEPA program has been fully implemented. Scenario B represents the effects by conducting more control measures beyond scenario A. The measures in Scenario B included the phase-out of 2-stroke...
motorcycles, promotion of hybrid vehicles and electric buses, and switch the coal-fired power plants into natural gas.

The ambient PM$_{2.5}$ concentration was evaluated by Community Multi-scale Air Quality modelling system (CMAQ) v4.6 along with the fifth-generation Pennsylvania State University - National Center for Atmospheric Research Mesoscale Model (MM5) ver. 3.7. The grid resolutions in the modelling work are 81 km $\times$ 81 km for domain 1 (covers East Asia), 27 km $\times$ 27 km for domain 2 (covers Southeast China and Taiwan), and 9 km $\times$ 9 km for domain 3 (covers Taiwan).

RESULTS AND DISCUSSIONS

Emission estimation of various scenarios were shown in Table 1. A clear tendency of emission abatement on primary PM$_{2.5}$, NOx, and SOx for scenario A and B was found. The emission reductions would be 13,870 tons/year (PM$_{2.5}$), 17,900 tons/year (SOx), and 158,220 tons/year (NOx) in scenario A. The reductions would be 18,760 ton/year (PM2.5), 59,500 tons/year (SOx), and 200,210 tons/year (NOx) for case B. These data indicated that the control measures could reduce the emissions significantly.

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Emissions (tons/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>Base Scenario</td>
<td>73,540</td>
</tr>
<tr>
<td>Scenario A</td>
<td>59,670</td>
</tr>
<tr>
<td>Scenario B</td>
<td>54,780</td>
</tr>
</tbody>
</table>

Table 1. Emissions of PM$_{2.5}$, NOx, and SOx in various scenarios

The results of PM$_{2.5}$ concentration simulation in different regions of Taiwan under various scenarios were shown in Figure 1. Annual average concentration of basic scenario is 14.2 µg/m$^3$ in northern Taiwan, 28.4 µg/m$^3$ in central Taiwan, and 29.9 µg/m$^3$ in southern Taiwan. These data also indicated the good performance of air quality modelling work in this study. The annual average concentration of PM$_{2.5}$ would be reduced by 14-23 % and 20-33 %, respectively, for scenarios A and B. The composition of airborne PM$_{2.5}$ is also shown in Figure 1. For the base scenario, the nitrate concentrations would be 1.22 / 4.64 / 5.58 µg/m$^3$ in northern, central, and southern Taiwan, respectively. The values of nitrate concentration would be 0.91 / 2.99 / 3.77 µg/m$^3$ for scenario A, and 0.80 / 2.49 / 3.13 µg/m$^3$ for scenario B. Both scenarios showed a clear improvement on nitrate concentration in airborne fine particulate matter. These results indicate that abatement of NOx emissions may result in significant improvement on airborne PM$_{2.5}$ concentration in Taiwan.
Figure 1. PM$_{2.5}$ concentration in different regions of Taiwan under various scenarios.

CONCLUSIONS

The result indicates that the TEPA program could not improve effectively the airborne PM$_{2.5}$ concentration to attain the air quality standard. The further reduction proposal of scenario B could improve the PM$_{2.5}$ concentration but it would not attain the standard either. More control measures to reduce much more emissions from various emission sources should be developed for attainment task.

ACKNOWLEDGEMENT

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REFERENCES

MULTI-YEAR LONG NEW PARTICLE FORMATION IN URBAN ENVIRONMENTS

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Keywords: urban new particle formation, particle number size distribution, particle number concentration, atmospheric nucleation.

INTRODUCTION

Ultrafine particles (UF, d<100 nm) have the largest contribution to the total particle number concentration on global scale (Kulmala et al., 2004). Their main sources include direct emissions (vehicular exhaust, heating, burning) and atmospheric nucleation and consecutive growth process (Wählin et al., 2001; Kulmala et al., 2013). New particle formation has been identified at various locations from clean sites to polluted environments (Brines et al., 2015). The urban atmospheric nucleation has been increasingly investigated due to the superposition of freshly formed particles with the already existing UF particles resulting high particle number concentrations (up to 10⁴–10⁵ cm⁻³) (Kumar et al., 2014).

METHODS

Particle number size distribution (PNSD) measurements were performed by Differential Mobility Particle Sizer (DMPS) in the diameter range of 6–1000 nm for 1 year in near-city background, and for 3 years in the city centre of Budapest, Hungary. The investigation of formation and growth rates were carried out for all years. The meteorological data and air pollutant concentrations were investigated between t₁ and t₂ time parameters (start and end time of the formation of particles) on nucleation days, and between average t₁ and t₂ time parameters on non-nucleation days for the 3-year long measurements in the city centre (Németh and Salma, 2014). K-mean analysis with Euclidean distance metric was used to investigate ca. 225,000 individual particle number size distributions. From 5 to 10 clusters were generated to separate the typical size distributions and atmospheric conditions.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Time interval</th>
<th>PNSD data coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>City centre</td>
<td>2008 Nov – 2009 Nov</td>
<td>94%</td>
</tr>
<tr>
<td>Near-city background</td>
<td>2012 Jan – 2013 Jan</td>
<td>94%</td>
</tr>
<tr>
<td>City centre</td>
<td>2013 Nov – 2014 Nov</td>
<td>98%</td>
</tr>
<tr>
<td>City centre</td>
<td>2014 Nov – 2015 Nov</td>
<td>94%</td>
</tr>
</tbody>
</table>

Table 1. Measurement sites and time intervals with data coverage in Budapest.

RESULTS AND CONCLUSIONS

The seasonal variation of nucleation frequency was determined separately for the city centre, and near-city background environments for years. The annual mean frequency of NPF events was 24%, 20% and 24% for the city centre and 28% for the background (Figure 1.). The inter-annual variability with a minimum in winter and two local maxima, one in spring and the other in autumn caused by favourable meteorological conditions or biogenic cycling.
The total particle number concentrations were $11.8 \times 10^3$, $9.7 \times 10^3$, and $9.3 \times 10^3 \text{ cm}^{-3}$ in the city centre, and showed slightly decreasing tendency during the years. The UF ratio had a similar pattern, resulted by the new particle formation frequency and the fluctuation of other anthropogenic sources. Some ordinary and substantial emission sources, such as boat traffic on rivers in cities or diesel-driven single heavy-duty tracks or buses, cause sudden and considerable changes in the concentration in an irregular or occasional manner. In the near-city background, the median total particle number concentration was $3.9 \times 10^3 \text{ cm}^{-3}$, and the UF contribution to the total concentration was 66% due to the lower traffic and local emission sources.

The correlation of $N_{0.25}$ with meteorological data and air pollutant concentrations were investigated. Slightly higher WS occurred on nucleation days which could be in relation with more intense air mass movements and boundary layer dynamics (Németh and Salma, 2014). The SO$_2$ concentration was not altered on nucleation and non-nucleation days which means that sufficient amount of SO$_2$ was always present for NPF in the lower troposphere (Salma et al., 2016). New particle formation did not take place above 84 µg m$^{-3}$ of NO, and anti-correlation was determined. The concentrations of NO$_2$ and PM$_{10}$ have no effect on the phenomena.

Eight clusters were determined for the city centre environment. Cluster 1 represented the clean atmospheric environment without new particle formation events. These size distributions were equally distributed among seasons with low concentration of air criteria pollutants and total particle concentration ($N=5 \times 10^3 \text{ cm}^{-3}$). Cluster 2 was influenced by emission sources resulting strong Aitken-mode. The growth of UF particles originated from atmospheric nucleation was in the Cluster 3, which was most frequent in spring. The modest increase of Aitken-mode particles were present in Cluster 4 which was the second most frequent group of clusters representing a general condition of atmospheric environment in the city centre without NPF. The extreme strong burst of new particle formation (Cluster 5, UF/N=0.96) was dominant in spring with 57%. This cluster had the same number median mobility diameter with Cluster 6, which represented the early stage of new NPF with the same seasonal dominance. The latter 2 clusters
were associated with the highest ozone levels (43 and 37 µg m⁻³, respectively) and low CO, NO and NO₂ concentrations. Cluster 7 contained the particle number size distributions having broad Aitken- and accumulation modes joined together with very low contribution of \( N_{6-25} \) to the increased total particle number concentration (\( N_{6-25}/N=0.22 \)). This group and Cluster 8 had increased PM₁₀ concentrations. The cluster 8 had also a distinct peak in the accumulation mode and was dominant in winter (40%). The latter two groups had the general characteristics of the polluted environment without new particle formation. The SO₂ did not show considerable change in the city centre. Cluster 1 and 2 contained the size distributions originating from new particle formation event with the highest contribution of UF particles to the total particle number concentration. Photochemical activity played an important role according to the highest ozone concentrations, and the anthropogenic markers NOₓ and CO were significantly low. The occurrence of cluster 1 and 2 was 47% and 42% in spring, which is in line with the annual nucleation frequency. Cluster 3 represented the clean air mass with low particle number and air pollutant concentrations. This cluster was dominant with 62% of all size distributions and did not show seasonal dependency. The group of more polluted atmospheric environment (Cluster 4) occurred mostly on non-nucleation days in autumn and in winter. It showed the increasing significance of biomass and wood burning for residential heating. Cluster 5 contained remarkable Aitken-mode with high UF/N ratio with elevated O₃ and NOₓ concentrations leading to a mixed, photochemically active and emission-driven group of size distributions. The last cluster contained the regional particles in the accumulation mode, and so the total and ultrafine particle number concentration was low. This group was the second most frequent (22%) and occurred mostly on non-nucleation days in autumn and in winter. However, the SO₂ concentration did not show strong variation for all clusters.

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REFERENCES


CHARACTERISTICS OF PM$_{2.5}$ FROM VINYL COMBUSTION

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Keywords: VINYL/PLASTIC, COMBUSTION, PM$_{2.5}$.

INTRODUCTION

The World Bank reported that world cities generate about 1.3 billion tones of solid per year, and this amount will largely increase to 2.2 billion tonnes by 2025. Li et al. (2012) reported that garbage burning is a commonly practice in disposing solid wastes in both developed and developing countries and open burning of solid wastes are major sources pf aerosols in South Asian countries (Kawamura and Pavulvuri, 2010). The purpose of this study is to determine PM 2.5 characteristics from vinyl combustion in a controlled setting.

METHODS

The study utilized a dual-cone calorimeter for the burning process of the vinyl samples. PM analysis was collected using a dust spectrometer (Grimm) and a pump with an attached tedlar bag was used for the collection. With the application of three heat fluxes (15, 25 and 50kW/m$^2$), the collection of different parameters were saved automatically and data were stored and analyzed.

RESULTS

As shown in figure 1, pm sizes of 0.35 and 0.45 μm have the highest concentration from the heat fluxes applied. The result also presented that usage of 50kW/m$^2$ produces the largest amount of PM concentration among the temperature.
CONCLUSIONS

Smaller PM sizes attaining larger value signifies a potential health risk of vinyl combustion exposure. Although, it is under laboratory conditions, the data could represent actual field burning. In addition, since several factors were not addressed, further research and data gathering is required.

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REFERENCES


CHARACTERIZATION OF PRIMARY ORGANIC AEROSOL OF DOMESTIC WOOD, PEAT, AND COAL BURNING

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Keywords: ACSM, WOOD, COAL, PEAT, SOLID FUELS.

INTRODUCTION

Ambient particulate matter (PM) adversely affects human health (Pope et al., 2002) and has a great influence on climate (O’Dowd et al., 2004). Direct Aerosol Mass Spectrometer (AMS) measurement of OA from various primary emissions can help understand the MS signatures of different primary OA sources and thus help the interpretation of AMS MS. To the best of our knowledge, direct ACSM, a compact version of AMS, measurements and comparison of domestic wood, peat, and coal burning have not been reported which should get more attention for their significant impacts on air quality in areas where these fuels are popular, e.g. Ireland and the UK.

METHODS

Wood, peat, and coal were burned in a typical residential stove in Ireland (Scheme 1). Characterization of PM emitted from burning these samples was conducted using an ACSM. OA was found to be the major contributor to the total sub-micro non-refractory (NR-PM1) aerosol particles. Unit mass resolution mass spectral signatures of OA from each fuel type were studied and compared. These directly ACSM measured reference profiles were used to apportion the ACSM measured ambient OA in Dublin, Ireland to estimate their relative contribution to air pollution and characterize their emission and formation process by constraining the profiles with ME-2 when running PMF.

![Diagram of the measurement system](attachment:Diagram.png)

Scheme 1. Schematic of Irish residential solid fuel combustion and ACSM measurement system

RESULTS

Averaged normalized ACSM unit mass resolution (UMR) mass spectra (MS) of OA particles obtained for dry wood, peat, and coal are shown in Figure 1. All three MS are dominated by CₙH₂ₙ₊₁ (29, 43, 57, 71…).
and C_{n}H_{2n+1} (27, 41, 55, 69…), indicating the large contribution from saturated alkanes, alkenes, and also possible cycloalkanes in the primary OA emissions from wood, peat, and coal. However, the MS profile patterns and signals at specific m/z (e.g. m/z 60) of different fuels vary significantly corresponding to the composition of the fuels. For example, the most prominent ion in wood burning aerosol MS profile is the signal at m/z (mass to charge ratio) 29, followed by m/z 43 while m/z 43 is the most abundant ion in peat emissions, followed by m/z 29. In contrast, m/z 43 and m/z 41 are the most abundant ions in coal emissions MS. In addition, there was a higher contribution from heavier ions (in the range of m/z > 120) in the coal emission spectra most likely from PAH emissions if compared to the peat and wood spectra.

Figure 1. Normalized mass spectra of organics from the combustion of (A) dry wood; (B) peat briquettes; (C) smoky coal.

Figure 2. Time series of ACSM, aerosol chemical speciation monitor, measured non-refractory particulate sub-micron matter species (NR-PM1, i.e. organics, sulfate, nitrate, ammonium, and chloride) before and after the high pollution event on 22nd Jan, 2017 in Dublin, Ireland. Relative contribution of ACSM measured species emphasize the importance of organic which accounts for 68% of total NR-PM1. Nitrate accounts for 17% of total NR-PM1, and was elevated throughout the pollution events indicating a regional source.
Real time measurements of NR-PM1 capture pollution events with peak concentration of 207 µg/m3 occurring at around 21:00 at UCD, Dublin, an urban background monitoring site (Figure 2). The night time pollution corresponds to domestic heating activities. As possible source candidates of OA, wood, peat, and coal, as well as oil burning emission were evaluated using PMF source apportionment technique to assess their contribution to the extreme air pollution events. For source apportionment of OA, we take advantage of ME-2 which can direct the PMF analysis to environmentally reasonable solutions by constraining the priori ACSM derived source profiles of peat, coal, and wood, as well as oil (HOA) from Crippa et al. (2013). A small a-value of 0.1 (i.e. 10% variation in profile) was applied due to the fact that most primary OA were freshly-emitted, with peak concentrations occurring at the early nighttime and thus should have small variation from the ACSM derived fingerprints (Figure 3). Due to the lack of possible tracer marker for each type of domestic fuel combustions, the best a-value will be further investigated.

![Figure 3. Factor profiles (mass spectra) of 5-factor ME-2 solution.](image)

ACSMM-PMF results show the importance of solid fuel burning during the pollution events, with the combined contribution of coal, peat, and wood of 78% to the total OA (Figure 4). Among solid fuels, peat was the dominant OA factors and peaked at around 21:00 in the evening, accounting for 41% of total OA.
which is consistent with the popularity of peat and International Energy Agency (2013) data that shows peat was mostly consumed solid fuel in Ireland. The contribution of coal was only around 8%, which is consistent with the ban on sales of smoky coal in Dublin. OOA was relatively stable compared to primary OA with elevated concentration during early night which might from the condensation of volatile organic matter. OOA is prevalent throughout the day while all primary factors fell to background levels during the day. The behavior of OOA indicates its formation process needs favorable conditions such as time and temperature. Back trajectory of air masses shows OOA might come from mainland Europe.

ACKNOWLEDGEMENTS

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REFERENCES


ANALYSIS OF AEROSOL CHEMICAL COMPOSITION
MEASURED AT URBAN AND RURAL SITES IN JAPAN

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Keywords: Q-AMS, LONG-RANGE TRANSPORT, POSITIVE MATRIX FACTORIZATION.

INTRODUCTION

Air Pollution emissions in East Asia have increased due to the rapid economic growth in this region (Ohara et al., 2007; Lu et al., 2010; Kurokawa et al., 2013). Since Japan is located at the downwind side of the Asian continent, transport of gas and aerosol prevails due to the seasonal monsoon in winter and spring. Among air pollutants, aerosol is considered to cause adverse effect on human health. In order to take mitigation and/or adaptation plan, it is necessary to understand the chemical composition of the aerosol. The chemical composition of aerosol reflects their transport process (Takami et al., 2016). Fukuoka (Fukuoka prefecture, 33.5°N, 130.3°E) is one of the largest cities in Japan located at northern part of Kyushu, and it is influenced by both local and long-range transported aerosols. Fukue Island (Nagasaki prefecture, 32.8°N, 128.7°E) is a rural area, located in the East China Sea approximately 190 km west of Fukuoka, and it is also influenced by long-range transported aerosol. Cape Hedo (Okinawa prefecture, 26.7°N, 128.3°E) is also rural area, faced to the East China Sea approximately 650 km south of Fukue Island, and it is also influenced by long-range transported aerosol. We measured aerosol chemical composition using Aerodyne aerosol mass spectrometers in Fukuoka, Fukue Island, and Cape Hedo, simultaneously. A positive matrix factorization (PMF) method was applied to analyze the organic composition, which is also considered to reflect their transport process. We compared the aerosol chemical composition and aging of organic aerosol at these three sites to understand the impact of long-range transported aerosol on the urban and rural atmosphere in Japan.

METHODS

We measured aerosol chemical composition at three different sites as mentioned above. Cape Hedo and Fukue Island are the rural places, where there are no major industries and populations are small. Cape Hedo is at longer distance from the Asian continent than Fukue Island, and we expect to see more aged aerosol. Fukuoka is one of the largest cities in Japan. Its population is about 1.5 million and there are large commercial and industrial areas. We expect to see the mixture of particles for local and long-range transported aerosol. Figure 1 shows the location of the three sites.

We used quadrupole-type aerosol mass spectrometer (Q-AMS, Aerodyne Research Inc.) and aerosol chemical speciation monitor (ACSM, Aerodyne Research Inc.). The details of Q-AMS and ACSM are
found in the literature (Jayne et al., 2000; Jimenez et al., 2003; Takami et al., 2005; 2007; Ng et al., 2011). Briefly, the sample air was introduced through the aerodynamic lens, which was separated into gas and aerosol and particle beam formed. The particle beam hit a vaporizer, which was set at 600 °C, and where non-refractory species in the aerosol were vaporized. The vaporized molecules were ionized by the electron impact method with 70eV. The ions were analyzed using a quadrupole type mass spectrometer. The particle mass was calibrated using ammonium nitrate particles with 350 nm (Q-AMS) or 300 nm (ACSM) diameters, and the ionization efficiency and the relative ionization efficiency were determined. The size calibration was carried out using polystyrene latex particles whose size is known. A cyclone was attached at the inlet pipe to cut the coarse particles. At Cape Hedo and on Fukue Island, the height of the inlet was about 4 m from the ground and that in Fukuoka was about 15 m from the ground since we set Q-AMS in the 4th floor of the building. The observation periods were around March 2016. Organic data obtained by Q-AMS and ACSM were analyzed by the PMF method using the PMF evaluation tool developed by Ulbrich et al. (2009). Mass concentrations of PM$_{2.5}$ were measured using a beta-ray absorption technique.

![Map of Japan with sites of interest](image)

Figure 1. Location of the three sites in Japan.

RESULTS AND DISCUSSION

Figure 2 shows time series of chemical composition measured by Q-AMS and PM$_{2.5}$ mass concentration in Fukuoka. Total mass concentrations of chemical components showed a similar variation with PM$_{2.5}$ mass concentration. While sulfate and organics were major components in all sites, nitrate was more significant in Fukuoka than that on Fukue Island and at Cape Hedo (Figure 3).

![Time series graph](image)

Figure. 2 Time series of Q-AMS results and PM$_{2.5}$ observed at Fukuoka.
This indicates that all sites were influenced by the long-range transport of air pollution and SO₂ emitted in China, which was chemically transformed to sulfate during long-range transport. We reported that high concentrations of sulfate were observed when the air mass was transported from China to Cape Hedo and Fukuoka Island in previous studies (Takami et al., 2005; 2007). The fraction of nitrate on Fukuoka Island was lower than that at Cape Hedo because of short transport time. Nitrate accounted for a relatively high value in Fukuoka because there was some local emission for example vehicle exhaust (Takami et al., 2016; Yoshino et al., 2016).

Figure 3. Breakdown of chemical composition at Fukuoka, Fukue and Cape Hedo. NH₄: ammonium, NO₃: nitrate, SO₄: sulfate, Chl: chloride, Org: organics.

The aging of organics was analyzed by a Positive Matrix Factorization method. At Cape Hedo and on Fukuoka Island, organics were divided into two factors. The mass spectra of the first component show the highest signal at m/z = 44 (COO fragment), considered to be well aged organics (low volatile oxygenated organic aerosol, LV-OOA) as Factor 1. The second one shows the relatively higher signal at m/z = 41 (C₅H₃ fragment), 43 (CH₃CHO, C₅H₆ fragments) with respect to m/z = 44 signal (semi volatile oxygenated organic aerosol: SV-OOA), considered to be partly aged organics, and m/z = 55, 57 (C₆H₇, C₇H₈ fragments) considered to be fresh organics (hydrocarbon-like organic aerosol: HOA) as Factor 2. In Fukuoka, organics were divided into 3 factors as LV-OOA (m/z = 44 as COO fragments), SV-OOA + HOA (m/z = 43 as CH₃CHO, C₅H₆ fragments), and HOA (m/z = 41, 55, 57 as C₅H₇, C₆H₈, C₇H₈ fragments). Figure 4 shows that mass fraction of LV-OOA, SV-OOA, and HOA at each site. The fraction of LV-OOA is dominant at Cape Hedo compared with Fukuoka Island and Fukuoka. This indicates that the air quality at Cape Hedo is mainly influenced by long-range transport of air pollution because organics emitted in the Asian continent were well aged and transformed to LV-OOA during long-range transport. On Fukuoka Island, the fraction of LV-OOA is slightly higher than SV-OOA + HOA. It means that the air quality on Fukue Island is influenced by long-range transport of air pollution with short transport time. In Fukuoka, LV-OOA is also dominant, while independent HOA fraction is observed.

Figure 4. Mass fraction of LV-OOA, SV-OOA, and HOA at the three sites.
These indicate that the air quality of Fukuoka is influenced by both long-range transported air pollution from Asian continent and local air pollution from Kyushu area, Japan.

CONCLUSIONS

We measured aerosol chemical composition at three different sites in Japan. The direct comparison was made for chemical composition and aerosol observed at Cape Hedo was more aged and influenced strongly by long-range transported aerosol compared to that in Fukuoka and on Fukue Island. It was also influenced by long-range transported aerosol on Fukue Island with short transport time. The air quality of Fukuoka was influenced both by long-range transported and local air pollution.

ACKNOWLEDGEMENTS

We thank Dr. T. Hikida (Shoreline Research, Inc.) and Mr. Y. Takeda (NIES) for their support of the observation at Cape Hedo. This work was supported by Environment Research and Technology Development Fund of the Ministry of Environment, Japan (Grant No. 5-1452, 2-1403).

REFERENCES


TWO YEARS OF NEAR REAL-TIME MEASUREMENTS OF CARBONACEOUS AEROSOLS IN URBAN BEIJING, CHINA: SEASONAL VARIATIONS, METEOROLOGICAL EFFECTS AND SOURCE ANALYSIS

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Keywords: OC, EC, PM\(_{2.5}\), SECONDARY ORGANIC CARBON, SOURCE ANALYSIS.

INTRODUCTION

Considering that OC and EC are closely associated with public health, atmospheric environment and climate change, worldwide attention has been paid to study carbonaceous aerosols. A quantitative description on the variations in Beijing is vital for constraining the role of carbonaceous aerosols in global climate models because Beijing is located in a large source area in northern China (Han et al., 2009; Bond et al., 2012). In this study, the OC and EC levels in PM\(_{2.5}\) were observed in the central zone of Beijing, where energy structure and policy change a lot. The OC and EC pollution characteristics and their seasonal and diurnal variations are presented. The relationship between OC and EC and meteorological parameters is explored. The effects of meteorological parameters, in particular relative humidity and temperature on the OC and EC variations were investigated. The potential source areas lead to high concentrations of OC and EC during the four seasons via potential source contribution function (PSCF) analysis.

METHODS

OC and EC in PM\(_{2.5}\) were measured with a thermal optical transmission OC/EC analyzer (Model 4, Sunset Laboratory Inc. Oregon, USA). PM\(_{2.5}\) was determined with a synchronized hybrid ambient real-time particulate monitor (SHARP 5030, Thermo-Fisher Scientific (TE), Massachusetts, USA), which is a US EPA Federal Equivalent Method analyzer. The NO\(_x\), SO\(_2\), CO and O\(_3\) were simultaneously measured using NO/NO\(_x\) analyzers (TE, 421), SO\(_2\) analyzers (TE, 431), CO analyzers (TE, 481) and O\(_3\) analyzers (TE, 49C), respectively. The potential source contribution function (PSCF) is then calculated as the ratio of the number of points with concentration higher than a threshold value \((m_0)\) to the total number of points \((n_0)\) in the \(j\)th grid cell.

CONCLUSIONS

A comprehensive analysis of OC and EC was performed at a data resolution of 1 h at an urban site in Beijing from January 2013 to December 2014. The following conclusions were obtained. Annual mean OC and EC concentration were lower than or comparable with previous studies. It suggests that progressive usage of clean energy in the residential areas and effectively controlling of diesel vehicles, small stoves and biomass burning improve air quality in spite of roaring rise of vehicle population. OC and EC concentrations increased with the increase of PM\(_{2.5}\) concentrations while its ratio to PM\(_{2.5}\) mass varied inversely. Two-peak diurnal variations were observed for OC and EC due to morning rush hour and the rule that HDV and HDDT are only allowed from midnight to early morning in Beijing. The high potential source areas of OC and EC were mainly located to the S and SW of Beijing. A common high potential source area to the SW of Beijing, along the Taihang Mountains, was observed during all seasons. In addition, local emission is more important in winter.
ACKNOWLEDGEMENTS

This work was supported by Ministry of Science and Technology of China (2016YFC0202701) and the Strategic Priority Research Program (B) 404 of the Chinese Academy of Sciences (Grant XDB05020501 & XDB05030207).

REFERENCES


OBSERVATIONS OF NEW PARTICLE FORMATION IN SUBTROPICAL HONGKONG

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Keywords: New particle formation; nucleation mode particle burst; Precursors

INTRODUCTION

Intensive field measurements were conducted from 25 October to 29 November in 2010 near the summit of Mt. Tai Mo Shan (Mt.TMS; 640 m a.s.l) and from December 2010 to January 2011 at an urban site (Hung Hom; HH) in Hong Kong. The particle number (PN) size distributions were characterized and the new particle formation (NPF) events were classified based on their strength and growth of geometric mean diameter (GMD). Moreover, the favorable meteorological conditions and possible mechanisms for the nucleation and growth of new particles were discussed by analyzing concurrently-observed meteorological parameters, gaseous pollutants, major hydrocarbons (e.g., isoprene, α-/β-pinenes, myrcene, limonene and aromatics), and carbonyl compounds i.e., formaldehyde, acetaldehyde and acetone. A number of NPF case studies in rural area demonstrated that NPF is typically favored under the conditions of low pre-existing aerosols. As such, the elevated background concentration of aerosols in polluted locations appears to suppress the particle nucleation. Nevertheless, the nucleation mode particle bursts were still observed in polluted environments and most of the studies have related the bursts to polluted plume with unusual high levels of primary pollutants i.e., SO₂, NOₓ and CO during daytime and nighttime.

METHODS

- Sampling site- Mt.TMS (rural site)

Mt. TMS is claimed to be Hong Kong's most misty area due to the high daily cloud coverage. Our monitoring site was located at the waist of Mt. TMS near the mountain summit (22.405°N, 114.118°E, about 640 m a.s.l.) (see Figure 1). Surrounding the foot of the mountain are urban centers with a population of 2.23 million. To the southwest is the newly-developed residential area of Tung Chung. To the west are the Tuen Mun residential areas and to the south is the South China Sea. To the north and northeast are the city clusters of the inland Pearl River Delta (PRD) region. The prevailing north/northeast synoptic winds in October – November bring polluted air on some days and clean air on some other days from inland PRD and eastern China coast to the sampling site, depending on the weather conditions at upwind locations.
Sampling site- Hung Hom (urban site)

HH site was on the rooftop of a building in the campus of Hong Kong Polytechnic University at Hung Hom, Kowloon (22.3° N, 114.177° E, about 40 m a.s.l) (Figure 1). This site was significantly affected by heavy traffic as it was located near main roads and cross-harbor tunnel (CHT), about 50 m away from the Hong Chong Road (about 30 m wide) with four lanes in each direction. The daily average number of vehicles passing through the CHT was about 122,000 in December 2010 - January 2011. The traffic peaks appear at 08:00 - 09:00 in the morning and 17:00 - 18:00 in the afternoon and evening. To the northeast of the sampling site, there are two funeral parlors with a distance of ~500 m. To the southwest and southeast is the Victoria Harbour. Hence, the study area could be affected by traffic emissions, incineration from the funeral parlour and marine vessel emissions.

![Figure 1](image)

**Figure 1** Locations of Hong Kong and the sampling sites.

Sampling techniques

**SMPS+CPC:** Particle size distributions (PSD) in the range of 5.5 to 350 nm were continuously measured by a Scanning Mobility Particle Sizer and a Condensation Particle Counter (model 5.400, GRIMM, Germany) system with 44 size bins at 4-min scan intervals.

**Trace Gases:** Ozone (O₃) was measured using a commercial UV photometric instrument (Advanced Pollution Instrumentation (API), model 400E) that had a detection limit of 0.6 ppbv.

Sulfur dioxide (SO₂) was measured by a pulsed UV fluorescence (API, model 100E), with a detection limit of 0.4 ppbv and 2-σ precision of 0.5% for ambient levels of 50 ppbv (2-min average).

Carbon monoxide (CO) was measured with a gas filter correlation, nondispersive infrared analyzer (API, Model 300E) with a heated catalytic scrubber (as purchased) to convert CO to carbon dioxide (CO₂) for baseline determination. The detection limit was 30 ppbv for a 2-min average. The 2σ precision was about 1% for a level of 500 ppbv (2-min average) and the overall uncertainty was estimated to be 10%.
Nitric oxide and NO\textsubscript{x} were detected with a chemiluminescence NO-NO\textsubscript{2}-NO\textsubscript{x} analyzer (API, Model 200E). The analyzer had a detection limit of 0.4 ppbv.

**Volatile organic compounds (VOCs) and carbonyl compounds:** Ambient VOC samples were collected using cleaned and evacuated 2-L electro-polished stainless steel canisters. A flow-controlling device was used to collect 1-h integrated samples. Hourly samples were consecutively collected from 0900 to 1600 with additional samples collected at 0000, 0300, 0700, 1800 and 2100 per day.

Carbonyl samples were collected on the same sampling days using the silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH). Air samples were drawn through the cartridge at a flow rate of 0.8–0.9 L min\textsuperscript{-1} for 120 min (2 hours); the flow rate through the cartridges was monitored with a rotameter which was calibrated before and after each sampling. An O\textsubscript{3} scrubber was connected to the inlet of the DNPH–silica cartridge to prevent interference from O\textsubscript{3}.

**Meteorological parameters:** Temperature, relative humidity, solar radiation, UV light, wind speed and direction were recorded during the sampling periods.

**CONCLUSION**

The NPF events were observed on 12 out of 35 days at Mt.TMS and 7 out of 30 days at HH during the intensive sampling sessions. At the Mt. TMS site, the diurnal variation of nucleation mode particle number concentration (N\textsubscript{nucl}) showed a significant contribution of NPF to elevated N\textsubscript{nucl} via photochemical reactions. While at the HH site, the diurnal variation analysis indicated that N\textsubscript{nucl} was influenced by primary emissions in early morning and at night, and was attributed to the NPF at noon. Weather conditions with strong solar radiation, high wind speed, low RH, and low condensation sink were found to be favorable for the NPF in the atmosphere of both rural and urban areas (see Figure 2, a typical NPF). In rural area, it was found that the formation rate of 5.5 nm particles had a power-law dependence on sulfuric acid concentration, with the typical power between 1 and 2, and the contribution of sulfuric acid vapor to the particle growth rate ranged from 9.2% to 52.5% on these NPF event days. Beside sulfuric acid vapor, monoterpenes were identified as the most important BVOC species related to the particle growth.

Differently, the NPF events occurred at the urban site showed power-law correlations with H\textsubscript{2}SO\textsubscript{4} vapor concentrations but with the exponents larger than 2. It indicated different mechanisms of NPF at these two sites, and probably more complicated formation processes at the urban site than at the rural site. In addition, 4 nucleation mode particle burst events (see Figure 3, a burst event occurred at nighttime) were identified during the 30-day sampling campaign at the urban site. The N\textsubscript{nucl} in the burst events had close correlation with NO\textsubscript{x} and SO\textsubscript{2}, implying that combustion sources with high sulfur-containing fuel might be the dominant emissions of the nucleation mode particles. Weather conditions with low wind, high RH and low temperature/solar radiation were often observed in these burst events. The calm wind was not beneficial to the dispersion of nucleation mode particles directly emitted from the combustion sources, whereas the high RH and low temperature enhanced the nucleation and condensation of the gaseous precursors emitted from the combustion sources to form nucleation mode particles.
Figure 2 Contour plots of airborne pollutants on 28 October 2010 at Mt.TMS. From top to bottom, the parameters are: PSD; Wind; Solar radiation; T and RH; N_{Ait} and N_{acc}; N_{nuc} and condensation sink (CS); NO and SO\textsubscript{2}; O\textsubscript{3} and CO.

Figure 3 The nucleation mode particle burst event on 14/15 January 2011 at the HH site. From top to bottom: PSD; solar radiation; wind; T and RH; NO and NO\textsubscript{2}; O\textsubscript{3} and SO\textsubscript{2}; CO and CS.
Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China

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Keywords: HAZE POLLUTION EPISODE, AIR POLLUTION COMPLEX, METEOROLOGY

INTRODUCTION

In January 2013, a long-lasting episode of severe haze occurred in central and eastern China. It has attracted attentions from all sectors of society. Five haze pollution episodes were identified in the Beijing-Tianjin-Hebei (Jing-Jin-Ji) area; the two most severe episodes occurred during 9–15 January and 25–31 January. During these two haze pollution episodes, the maximum hourly PM$_{2.5}$ mass concentrations in Beijing were 680 and 530 $\mu$g m$^{-3}$, respectively. The process and evolution of haze pollution episodes in other major cities in the Jing-Jin-Ji area, such as Shijiazhuang and Tianjin were almost the same as those observed in Beijing. The external cause of the severe haze episodes was the unusual atmospheric circulation, the depression of strong cold air activities and the very unfavorable dispersion due to geographical and meteorological conditions. However, the internal cause was the quick secondary transformation of primary gaseous pollutants to secondary aerosols, which contributed to the “explosive growth” and “sustained growth” of PM$_{2.5}$. Particularly, the abnormally high amount of nitric oxide in the haze episodes, produced by fossil fuel combustion and vehicle emissions, played a direct or indirect role in the quick secondary transformation of coal-burning sulphur dioxide to sulphate aerosols (He et al., 2014).

METHODS

Observation sites in the CARE-China network were equipped with RP1400-PM$_{2.5}$ or RP1405-PM$_{2.5}$ (Thermo-Fisher Scientific, USA), which provide a continuous direct mass measurement of particulates by utilizing a tapered element oscillating microbalance (TEOM). NO$_x$ was measured using a chemiluminescence NO$_x$ analyser (Model 42i, Thermo-Fisher Scientific, USA), O$_3$ was measured using a UV photometric O$_3$ analyzer (Model 49i, Thermo-Fisher Scientific, USA), SO$_2$ was measured using a pulsed fluorescence SO$_2$ analyzer (Model 43i, Thermo-Fisher Scientific, USA) and CO was measured with a non-dispersive infrared analyzer (Model 48i, Thermo-Fisher Scientific, USA). The non-refractory submicron (NR-PM$_{1}$) aerosol species including organics, sulphate, nitrate, ammonium and chloride were measured using a HR-ToF-AMS at an urban site in Beijing.

CONCLUSIONS

Atmospheric circulation, local meteorological factors, and the structure of the boundary layer, together with specific geographical conditions, were unfavourable for pollutant diffusion. The abnormally high amount of NO$_x$ during the haze episodes, produced by fossil fuel combustion and vehicle emissions, played either a direct or indirect role in the rapid secondary transformation of SO$_2$ into sulphate aerosols. As haze pollution becomes a regional atmospheric pollution problem, synchronous emission abatement policies that are based on integrated planning should be implemented in stages to improve the regional air quality throughout central and eastern China, especially for the Jing-Jin-Ji area.

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REFERENCES

IMPACT OF REGINAL MICROCLIMATE AND PM2.5 CONCENTRATION ON SUB-URBAN ATMOSPHERIC VISIBILITY

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Keywords: ATMOSPHERIC VISIBILITY, PM2.5, MICROCLIMATE, SUB-URBAN.

INTRODUCTION

Regional microclimate and air pollution can lead to haze such as Figure 1. In this study, the level of environmental visual quality is quantified by atmospheric visibility observations. Digital visibility indicators and data base was established to clarify the straight-line distance of the targets by high frequency extraction of sub-urban images. Combined with the microclimatic conditions and PM2.5 monitoring, the relative impact of weather change or air pollution on atmospheric visibility, and the relationship between continuous maps of atmospheric environment and visual quality of landscape can be also clarified. In addition, this study also carried out statistical analysis on the relationship of PM2.5 temporal distribution and visibility. The main spatial and temporal distribution pattern of PM2.5 is explored, and a high correlation is obtained.

Figure 1. The regional haze in the special microclimatic condition of the central Taiwan.

METHODS

A digital mathematic matrix, f (x, y), is used to denote the spatial coordinates of environmental points, as well as the relative brightness (or gray level). Under the condition that the environmental image is segmented, its monochrome type can provide sufficient data for the visibility analysis and also simplify the processing procedure for digital model of visibility. The digitization of the amplitude of the image function is called grayscale quantization. Three filters of image high frequency and a processor of image degradation were used to develop the whole image analysis program without the dependency on the ideal targets (Luo et al., 2005a; Luo et al., 2005b; Luo et al., 2011). The equipment components of the image sampling system consist of a normalized digital camera, a support shaft, a signal transmission and central processing units (including a driver) which are subjected to chromatic aberration correction. The
environmental scene can be recorded, thus a wireless transmission space grid combined with the long distance visibility monitoring system can be established as a mesoscale environmental image monitoring system.

CONCLUSIONS

The monitoring data of PM2.5 and atmospheric visibility were collected from different monitoring stations for the sub-urban meteorological factors. The relative factors such as relative humidity, temperature and wind speed were selected. The analysis was based on the time series and the time period was divided into short (single day) and long (several weeks) periods. The results found delayed inverse relationship between PM2.5 concentration and wind speed happened. The relationship between digital visibility index and the wind speed showed a delayed variation. Regional visibility and wind speed showed a significant inverse relationship.

ACKNOWLEDGEMENTS

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REFERENCES

Development of WRF/Chem model system in central China and its application to study the regional PM$_{10}$/PM$_{2.5}$ characteristic and transportation over Henan

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Keywords: Particulate matter, WRF/Chem, Regional transportation, Contributions ratio

INTRODUCTION

In recent years, frequent dust-haze pollution in most areas of China, with large scope of influence and heavy pollution level, causes a wide attention at home and aboard. Atmospheric particulate matter is one of the main factors of haze formation, especially fine particles (PM$_{2.5}$) have a strong scattering and absorbing effect on visible light, which leads to a decrease of visibility and influences global climate change through direct and indirect effects, and they are also easy to adsorb metal ions and other toxic substances which seriously affect the quality of atmospheric environment and human health. Therefore, development of regional air quality forecasting system and provision of timely and accurate haze and other environmental meteorological forecast information are of great significance to protecting people's lives and health. At the same time, air pollution is of complex and regional characteristics, which is regional pollution phenomenon caused by transport of extraneous air pollution under the background of special weather conditions. Analysis and prevention of source of atmospheric particulates are the major problems all over the world and difficult problems urgently to be solved.

METHODS

In this research, regional refined emission source data were used to fuse the MIX Asian emission inventory of Tsinghua University in 2012, and the central air quality numerical forecasting system was established based on WRF/Chem atmospheric chemistry model. In recently two years, the result from forecast verification shows that forecast of the model system for variation trend of PM$_{10}$, PM$_{2.5}$, SO$_2$, NO$_2$, CO concentration and error stability are in good condition, and average absolute percentage error (MAPE) is controlled at 20%- 40%. Based on this model, concentrations of atmospheric particulate matters in Henan Province and its surrounding areas were simulated. Scenario experiments of multi-group regional emission sources were designed to quantitatively assess contribution of artificial source emission to concentration of atmospheric particulate matters in Henan Provinces from six areas of Henan, Beijing/Tianjin/Hebei, Shandong, Shanxi, Anhui/Jiangsu and Hubei. And then pollution transport characteristics of three representative cities were studied with meteorological data.
CONCLUSIONS

The results show that:
(1) WRF/Chem can better simulate change trend of particulate matter concentration in Henan province in December 2015. The monthly mean correlation coefficients of PM$_{10}$/PM$_{2.5}$ of simulated concentration value by hour and monitoring value are 0.62 and 0.71 respectively; absolute error, root mean square error and average absolute percentage error are controlled within a reasonable range; the model has the ability to simulate distribution characteristics of atmospheric particulates in Henan Province.

<table>
<thead>
<tr>
<th>Average</th>
<th>$R$</th>
<th>RMSE</th>
<th>MAPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$ Daily average</td>
<td>0.74</td>
<td>35.06</td>
<td>34.31%</td>
</tr>
<tr>
<td>Hourly average</td>
<td>0.71</td>
<td>35.80</td>
<td>35.92%</td>
</tr>
<tr>
<td>PM$_{10}$ Daily average</td>
<td>0.72</td>
<td>42.63</td>
<td>30.24%</td>
</tr>
<tr>
<td>Hourly average</td>
<td>0.68</td>
<td>43.71</td>
<td>32.70%</td>
</tr>
</tbody>
</table>

(2) Based on evolution characteristics of various weather elements, we can see that particulate matters are gradually accumulated and concentration is increased steadily under the background of constant pressure and small ground wind speed. The temperature drops abruptly when the night fell and relative humidity increases, which leads to reduction of atmospheric boundary layer, and top thermal inversion layer is not conducive to proliferation of pollutants, hence these factors together lead to two consecutive haze weather in Henan Province.

(3) In winter (December 2015), the main factor influencing the concentration of PM$_{2.5}$/PM$_{10}$ in Henan Province is discharge within the province, and average contribution rate is 54.83% and 61.32% respectively. Contributions of pollution transportation to PM$_{2.5}$/PM$_{10}$ in Henan Province also occupy a large proportion. Average contribution rates of PM$_{2.5}$ from Beijing/Tianjin/Hebei, Anhui, Jiangsu, Shandong, Shanxi and Hubei were 11.95%, 11.69%, 7.95%, 7.4%, 4.3%, 10.42%, 10.03%, 7%, 6.89% and 3.8% respectively(Fig.1). The external transport rate of PM$_{2.5}$ is higher than that of PM$_{10}$, which shows that fine particles are more likely to have a long-distance transportation than coarse particles. Regional pollution sources are complex, and improving air quality in Henan Province is a problem that needs to be faced and resolved by the whole region.
(4) The sources of particulate matter in different cities in Henan Province are closely related to their geographical location, pollution discharge, wind direction and wind speed. The dominant wind direction of heavy polluted weather in Zhengzhou was east wind, followed by west wind, and the largest contribution to pollution is Henan. The dominant wind direction in Puyang City is the north wind and the south wind. The pollution contribution rate of Beijing/Tianjin/Hebei is the highest under the control of the north wind and the northeast wind, and the pollution contribution rate in Henan is the highest under the control of clam wind and south wind. The main wind direction of heavy pollution in Shangqiu City is north wind and northwest wind. At this time, the pollution contribution is the largest in Shandong Province, followed by Henan Province when the main wind direction of heavy pollution is south wind.

Fig. 1 The distributions of regional contributions to PM$_{2.5}$ concentration of Henan province

Fig. 2 The time series of hourly PM$_{2.5}$ concentration (black solid line above the horizontal line), regional hourly contributions (colorful dashed line under the horizontal line) and wind vectors at 10-m every 6 hours.
ACKNOWLEDGEMENTS

It is noteworthy that further simulations and observations are still necessary due to the uncertainties of emission sources and limited simulating capability of the model to the secondary particles.

REFERENCES


Development and preliminary application of environmental meteorology numerical model system in central China

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Keywords: air pollution; WRF/Chem; atmospheric boundary layer height.

INTRODUCTION

Abstract: In order to support central China environment meteorological prediction services, and protect environment reducing air pollution, the environmental meteorology numerical model system was developed basing on the regional chemical dynamical model (WRF/Chem). It could provide the numerical forecasting product of air quality for regional environment. The system was preliminary applied in numerical prediction of air pollution in Wuhan at present, and was compared with CUACE (CMA Unified Atmospheric Chemistry Environment) forecast products. In addition, an air pollution optimal control plan was discussed through this test. The results show that: The numerical simulation results of model system could validate the temporal variation and spatial distribution of the air pollutants concentration in Wuhan. The population correlation coefficients and the forecasting effectiveness of PM10, PM2.5, SO2, NO2, CO concentrations were credible, and the mean absolute percentage error (MAPE) was controlled in 20% ~ 40%. The O3 concentration correlation coefficient was satisfactory, but the forecast results appeared positive deviation in winter. Compared with CUACE forecast products of every 3 hours concentrations of six air pollutants in Wuhan from September 2014 to January 2015, WRF/Chem products was better. It means that WRF/Chem was more referential value for the air quality forecast in Wuhan. Furthermore, an optimal adjustment test for air pollution control was tentative discussed by changing hourly emissions of pollution source. It suggests that without reduction of daily total emission, the air pollutants concentration can be reduced to some extent by changing the diurnal variations of the emissions according to the characteristics of atmospheric boundary layer height at different times of the day. In the later, we will collect longer observation data in more cities, and evaluate the accuracy and stability of WRF/Chem system.
Figure 1. Nested domain setup of the model
Figure 2. The observed and forecasted hourly concentrations of air pollutants of 10 observation stations in Wuhan from September 2014 to January 2015

Figure 3. The observed and forecasted hourly concentrations of air pollutants of 10 observation stations in Wuhan from September 2014 to January 2015

Forecast verification methods:

\[ R = \frac{\sum_{i=1}^{N} (p_i - \bar{p})(o_i - \bar{o})}{\left( \sum_{i=1}^{N} (p_i - \bar{p})^2 \sum_{i=1}^{N} (o_i - \bar{o})^2 \right)^{1/2}} \]

\[ MB = \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i) \]

\[ MNB = \frac{1}{N} \sum_{i=1}^{N} \frac{(P_i - O_i)}{O_i} \]

\[ RMSE = \left( \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i)^2 \right)^{1/2} \]

\[ MAPE = \frac{\sum_{i=1}^{N} |P_i - O_i|}{\sum_{i=1}^{N} O_i} \times 100 \% \]
Table 1. Forecast verification results of daily mean concentrations of air pollutants in Wuhan from September 2014 to January 2015.

<table>
<thead>
<tr>
<th></th>
<th>PM$_2.5$/ug/m$^3$</th>
<th>PM$_{10}$/ug/m$^3$</th>
<th>SO$_2$/ug/m$^3$</th>
<th>NO$_2$/ug/m$^3$</th>
<th>CO/mg/m$^3$</th>
<th>O$_3$/ug/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>0.52</td>
<td>0.42</td>
<td>0.57</td>
<td>0.63</td>
<td>0.62</td>
<td>0.74</td>
</tr>
<tr>
<td>MB</td>
<td>-7.92</td>
<td>1.48</td>
<td>-2.91</td>
<td>-1.35</td>
<td>0.01</td>
<td>23.22</td>
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<td>MNB</td>
<td>0.12</td>
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<td>0.06</td>
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<tr>
<td>RMSE</td>
<td>39.5</td>
<td>52.2</td>
<td>11.3</td>
<td>18.4</td>
<td>0.32</td>
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<tr>
<td>MAPE</td>
<td>34%</td>
<td>32%</td>
<td>36%</td>
<td>24%</td>
<td>20%</td>
<td>60%</td>
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Table 2. CUACE forecast verification results of every 3 hours concentrations of air pollutants in Wuhan from September 2014 to January 2015.

<table>
<thead>
<tr>
<th></th>
<th>PM2.5/ug/m$^3$</th>
<th>PM10/ug/m$^3$</th>
<th>SO2/ug/m$^3$</th>
<th>NO2/ug/m$^3$</th>
<th>CO/mg/m$^3$</th>
<th>O3/ug/m$^3$</th>
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<tr>
<td>R</td>
<td>0.31</td>
<td>0.26</td>
<td>0.11</td>
<td>0.48</td>
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<td>0.59</td>
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<tr>
<td>MB</td>
<td>-38.6</td>
<td>-71.1</td>
<td>-0.52</td>
<td>-29.5</td>
<td>-0.8</td>
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<td>MNB</td>
<td>-0.27</td>
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<td>0.25</td>
<td>-0.37</td>
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<td>1.68</td>
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<tr>
<td>RMSE</td>
<td>69.23</td>
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<td>20.86</td>
<td>40.76</td>
<td>0.92</td>
<td>39.7</td>
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<tr>
<td>MAPE</td>
<td>44%</td>
<td>53%</td>
<td>50%</td>
<td>47%</td>
<td>57%</td>
<td>108%</td>
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Table 3. WRF/Chem forecast verification results of every 3 hours concentrations of air pollutants in Wuhan from September 2014 to January 2015.

<table>
<thead>
<tr>
<th></th>
<th>PM2.5/ug/m$^3$</th>
<th>PM10/ug/m$^3$</th>
<th>SO2/ug/m$^3$</th>
<th>NO2/ug/m$^3$</th>
<th>CO/mg/m$^3$</th>
<th>O3/ug/m$^3$</th>
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<tr>
<td>R</td>
<td>0.47</td>
<td>0.32</td>
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<td>MB</td>
<td>-18.83</td>
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<td>MNB</td>
<td>-0.06</td>
<td>0.98</td>
<td>0.03</td>
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<td>0.02</td>
<td>2.28</td>
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<tr>
<td>RMSE</td>
<td>53.06</td>
<td>67.75</td>
<td>18.93</td>
<td>26.79</td>
<td>0.53</td>
<td>33.81</td>
</tr>
<tr>
<td>MAPE</td>
<td>32%</td>
<td>35%</td>
<td>45%</td>
<td>28%</td>
<td>29%</td>
<td>109%</td>
</tr>
</tbody>
</table>

REFERENCES


MIXING LAYER HEIGHT AND THE IMPLICATIONS FOR AIR POLLUTION OVER BEIJING, CHINA

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Keywords: CEILOMETER, MIXING LAYER HEIGHT, AIR POLLUTION.

INTRODUCTION

The mixing layer is an important meteorological factor that affects air pollution. The atmospheric mixing layer height (MLH) was observed in Beijing from July 2009 to December 2012 using a ceilometer. By comparison with radiosonde data, we found that the ceilometer underestimates the MLH under conditions of neutral stratification caused by strong winds, whereas it overestimates the MLH when sand-dust is crossing. Using meteorological, PM$_{2.5}$, and PM$_{10}$ observational data, we screened the observed MLH automatically; the ceilometer observations were fairly consistent with the radiosondes, with a correlation coefficient greater than 0.9. Further analysis indicated that the MLH is low in autumn and winter and high in spring and summer in Beijing. There is a significant correlation between the sensible heat flux and MLH, and the diurnal cycle of the MLH in summer is also affected by the circulation of mountainous plain winds. Using visibility as an index to classify the degree of air pollution, we found that the variation in the sensible heat and buoyancy term in turbulent kinetic energy (TKE) is insignificant when visibility decreases from 10 to 5 km, but the reduction of shear term in TKE is near 70 %. When visibility decreases from 5 to 1 km, the variation of the shear term in TKE is insignificant, but the decrease in the sensible heat and buoyancy term in TKE is approximately 60 %. Although the correlation between the daily variation of the MLH and visibility is very poor, the correlation between them is significantly enhanced when the relative humidity increases beyond 80 %. This indicates that humidity-related physicochemical processes is the primary source of atmospheric particles under heavy pollution and that the dissipation of atmospheric particles mainly depends on the MLH. The presented results of the atmospheric mixing layer provide useful empirical information for improving meteorological and atmospheric chemistry models and the forecasting and warning of air pollution.

METHODS

To understand the characteristics of the mixing layer in the Beijing area, a single-lens ceilometer (CL31, Vaisala, Finland) was used to measure MLH in in the courtyard of the Institute of Atmospheric Physics, Chinese Academy of Sciences (39.974° N, 116.372° E) from 15 July 2009 to 16 December 2012. This instrument utilizes pulsed diode laser lidar technology (910 nm waveband) to measure the attenuated backscatter coefficient profile and then determine the MLH. For practical measurements, the time
resolution was set to 16 s, the vertical resolution was set to 10 m, and the measurement range was 7.7 km. Because the atmospheric aerosol concentration is relatively high in Beijing, the CL31 lens was cleaned with clear water every 3 days. The conventional meteorological data during the same period included temperature, RH, WS, and wind direction observations at 8, 15, 32, 47, 65, 80, 100, 120, 140, 160, 180, 200, 240, 280, and 320 m along the tower in a vertical direction, and the temporal resolution was 30 min. The detailed description is provided by Song et al. (2013). The sensible heat, latent heat, were observed using ultrasonic anemometers (CSAT3, Campbell Scientific, USA) and CO2/H2O sensor (LI-7500, LiCor Inc, USA). The total (285–2800 nm) and net (0.2–100μm) radiation were observed using pyranometer (CM11, Kipp & Zonen, Netherlands) and net radiometer (NR Lite2, Kipp & Zonen, Netherlands). All of these data were obtained on the meteorological tower at a height of 280 m and processed with a resolution of 30 min. The detailed description is provided by Song (2012) and Wang and Hu et al. (2012). The profiles of atmospheric pressure, temperature, RH, WS, wind direction, and ozone were observed using the meteorological radiosondes at the international standard weather station (39.484 N and 116.282 E) that is 10 km from the MLH measurement site. The ground observations of PM2.5 and PM10 during the same period were made by the ambient particulate monitor (RP1400a, Thermo Fisher Scientific, USA). The data were acquired at a time resolution of 5 min and processed with a resolution of 60 min. A detailed description is provided by Liu et al. (2014). Because PM data were occasionally missing, visibility was used as an index to classify the degree of air pollution. Visibility was obtained from the Department of Atmospheric Science, College of Engineering, University of Wyoming (http://weather.uwyo.edu/surface/meteorogram/), was measured by a visibility sensor (PWD12, Vaisala, Finland) with an accuracy of ±10 %.

CONCLUSIONS

Based on a comparison with radiosondes, we determined that the ceilometer underestimates the MLH during near-neutral stratification caused by strong winds and that it overestimates the MLH during dust crossing. By combining meteorological, PM2.5, and PM10 data, we screened the observation results for the MLH; the availability of the acquired data is close to 80 %. The screened ceilometer observations are fairly consistent with the meteorological radiosondes, with a correlation coefficient greater than 0.9 (Fig.1).

![Figure 1. Comparison of MLH between the ceilometer and radiosondes for convective (a) and stable (b) condition.](image)

Although the correlation between the daily MLH and visibility is very poor (Fig.2), the correlation between them is significantly enhanced when the RH increases (Table.1). The high correlation between the MLH and visibility under high RH indicates that humidity-related physicochemical processes is the primary source of atmospheric particles under heavy pollution, whereas the dissipation of atmospheric
particles depends primarily on the vertical diffusion capability, which is dominated by the atmospheric MLH.

![Graph showing correlation between MLH and visibility according to relative humidity in Beijing.](image)

Figure 2. Correlation between MLH and visibility according to relative humidity in Beijing.

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>Visibility (km)</th>
</tr>
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<tbody>
<tr>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>90+</td>
<td>60</td>
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<table>
<thead>
<tr>
<th>RH (%)</th>
<th>40&lt;RH≤50</th>
<th>50&lt;RH≤60</th>
<th>60&lt;RH≤70</th>
<th>70&lt;RH≤80</th>
<th>80&lt;RH≤90</th>
<th>RH&gt;90</th>
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</thead>
<tbody>
<tr>
<td>R</td>
<td>0.15</td>
<td>0.04</td>
<td>0.01</td>
<td>0.09</td>
<td>0.41</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Table 1. Correlation coefficients (R) between the MLH and visibility according to RH (%).

ACKNOWLEDGEMENTS

This work was supported by CAS Strategic Priority Research Program Grants (nos. XDB05020000 and XDA05100100), the National Natural Science Foundation of China (nos. 41230642 and 41222033). We also gratefully acknowledge the Department of Atmospheric Science, College of Engineering, University of Wyoming for the provision of the meteorological data used in this publication.

REFERENCES


A CANDIDATE MEASUREMENT SYSTEM FOR THE STANDARDIZED ROUTINE MONITORING OF PARTICLE NUMBER CONCENTRATION IN AMBIENT AIR

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Keywords: CPC, UFP, particle number concentration, standardized method

INTRODUCTION

Ambient air monitoring data is used to understand and reduce urban haze, to assess the effectiveness of abatement measures (e.g. low emission zones), for epidemiological studies, and to derive recommendations for future action plans. While PM$_{2.5}$ and PM$_{10}$ measurements have been standardized for a long time (e.g. DIN EN 12341:2014), this is not the case for ultrafine particles (UFPs). On the other hand there is a growing awareness that UFPs could have significant effects on human health or our climate, especially as they are frequently present in large numbers due to traffic, residential heating, and other processes. They are best quantified using condensation particle counters (CPCs) as their contribution to the mass of atmospheric particles (PM) is essentially insignificant. A number of European monitoring networks including NABEL (EMPA, 2000) and GUAN (Birmili, 2015) have added CPCs to supplement gravimetric air quality measurements with a time resolved measurement of particle number concentration. Comparing these data can be challenging when CPCs with different lower cut-offs (D$_{50}$), operating conditions or even working fluids are used. In addition, different sampling systems can lead to large differences especially due to particle losses.

METHODS

The European Committee for Standardization (CEN) developed the Technical Specification CEN/TS 16976 as a first step of harmonizing the continuous measurement of particle number concentration in ambient air. This Technical Specification was published in August 2016 and describes a standardized method by defining a set of requirements not only for the Condensation Particle Counter (CPC), but also for its sampling and conditioning system, the measurement procedure and the reporting of measurement results. The CPC must be an n-butanol instrument with no flow splitting and single count mode measurement. The performance criteria for the CPC include flow rate accuracy, a lower limit of detection (D$_{50}$) at 7 nm, low zero count rate and fast response time. The sampling system must ensure a relative humidity of the aerosol below 40% at the inlet of the CPC and particle losses to be less than 30% at 7 nm.

In 2016 TSI Inc. (Shoreview, MN, USA) introduced the model 3772-CEN CPC and the model 3772200 sampling system, both fully compliant with the proposed CEN/TS 16976. This CPC operates with a volume flow rate of 1.0 L/min and uses an optimized coincidence and dead time correction method to count particles in single count mode up to concentrations of 50,000 particles/cm$^3$ (Figure 1a). The counting efficiency is verified with sintered silver particles down to a D$_{50}$ of 7 nm (Figure 1b). The 3772-CEN CPC also includes a pulse height analyzer that monitorswick health, super-saturation state, and instrument status. The same technology of monitoring the pulse height of every signal has been used in CPC’s designed for automotive type approval testing according to Euro 5b/6 legislations for many years.

The custom-designed sampling system was designed to minimize diffusion losses of the airborne particles. It draws 16.67 L/min through a PM$_{10}$ inlet, of which 5 L/min are dried by a single-tube Nafion® dryer (Perma Pure LLC, Lakewood, NJ, USA). Additionally it offers up to 3:1 dilution and continuous
measurement of relative humidity, temperature and ambient pressure for automatic logging in the 3772-CEN CPC.

Figure 1. a) Linearity data shown for 4 units, black line shows 1:1 regression, b) Counting efficiency for silver particles that are generated with the evaporation/condensation method, measured by the World Calibration Centre for Aerosol Physics (WCCAP) at TROPOS in Leipzig, Germany

CONCLUSIONS

The European Committee for Standardization (CEN) developed the Technical Specification CEN/TS 16976 as a first step of harmonizing the continuous measurement of particle number concentration in ambient air. This normative document will facilitate data collection and comparison in the future as it defines the measurement procedure and the reporting of measurement results, as well as a set of requirements for the CPC and for the sampling system.

The new Model 3772-CEN CPC and its dedicated sampling system Model 3772200 (TSI Inc., Shoreview, USA) have been presented and it is shown that they fully comply with the requirements laid down in CEN/TS 16976.

The measurement system employs technology that has been used in vehicle type approval testing according to Euro 5b/6 for many years and will ensure high accuracy as well as very tight tolerances for atmospheric researchers. In addition to the performance characterization results we will also give examples of the use of these new instruments designed for the standardized, routine monitoring of particle number concentration in ambient air.

REFERENCES

DIN EN 12341:2014. Ambient air - Standard gravimetric measurement method for the determination of the PM10 or PM2.5 mass concentration of suspended particulate matter (2014)
EMPA. Technischer Bericht zum Nationalen Beobachtungsnetz für Luftfremdstoffe (NABEL), Dübendorf, Switzerland (2000)
PHASE CHANGE BEHAVIOR OF SALT AEROSOL IN A CFDC

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Keywords: ice formation, deliquescence, homogeneous freezing, continuous flow diffusion chamber.

INTRODUCTION

Since Rogers (1998) developed the first continuous flow diffusion chamber (CFDC) for measuring atmospheric ice nucleating particle concentrations, this instrument type has found widespread use for laboratory and field operation. Its original design was optimized for the simulation of mixed phase cloud type conditions above the homogeneous freezing limit (~ -35°C). At colder temperatures, buoyancy in the instrument may lead to non-ideal flow behavior and thus increase uncertainties in sample temperature and/or relative humidity (Richardson, 2009). To overcome these uncertainties and to expand the accessible temperature regime, it is common to test the instrument performance against the water activity based parameterization for homogeneous freezing developed by Koop et al. (2000). On the other hand, Richardson (2009) demonstrated that below -40°C the sample flow speed significantly influenced the detection limits of his CFDC, which was related to the relatively slow crystal growth during the short residence time of the sample (~ 5 to 10 s). This might impede the direct comparison to and calibration against experimental data derived on longer timescales.

As a mean to calibrate our instrument for use in freezing studies in the cirrus cloud temperature regime, we investigated the phase change behavior of simple inorganic salts. As particle deliquescence is a phase transition that is not kinetically hindered and leads to nearly instantaneous size increase (Martin, 2000), we used this transition for validation of sample temperature and relative humidity.

Figure 1. Schematics of the INKA working principle (Schiebel et al., in preparation).
OPERATION PRINCIPLE OF THE INKA INSTRUMENT

The new INKA (Ice Nucleation Instrument of the Karlsruhe Institute of Technology; Schiebel et al., in preparation) is a cylindrical type CFDC with a 100 cm ice nucleation and ice crystal growth section (see Figure 1). The inner and outer walls of the chamber are ice covered and held at different temperatures, causing a temperature and water vapor pressure gradient in the 1 cm gap between the walls. The aerosol sample flowing through the gap is surrounded by particle free sheath air, so that temperature and water vapor pressure at sample location can be calculated. As conditions are always supersaturated in relation to ice, ice nucleating particles can activate. Close to liquid water saturation, the concurrent activation of cloud condensation nuclei is likely. Cloud droplets are therefore evaporated in the subsequent 50 cm droplet evaporation zone of the instrument, where constant wall temperatures induce ice saturated vapor conditions.

At the outlet of the chamber, an optical particle counter (OPC) is used to count the ice crystals formed in the instrument. For the investigation of immersion freezing activation at temperatures above the homogeneous freezing limit, ice particles have usually grown to sizes that are clearly larger than those of non-activated aerosol or partly evaporated droplets. However, at lower temperatures, the reduced rate of ice growth might result in non-discernible size differences of ice crystals and interstitial aerosol and thus in a delayed detection of freezing onset.

INVESTIGATION OF DELIQUESCENCE AND FREEZING BEHAVIOR

Aqueous solutions of sodium chloride and ammonium sulfate have been aerosolized using an atomizer, dried by diffusion dryers, injected into a 4 m³ aerosol preparation chamber and then sampled by INKA. Size distributions of the aerosol particles have been measured continuously throughout the sampling period. The deliquescence and freezing behavior was investigated for temperatures ranging from -60°C to -35°C and for relative humidities from ice saturation to liquid water supersaturation.

Figure 2. INKA measurements of sodium chloride aerosol at -40°C (left) and -50°C (right). Total flow rate was 12.5 l/min. For each experiment, panel I shows the water vapor saturation ratios at aerosol location, panel II shows the data of the OPC and panel III gives the measured total particle concentrations and concentrations above a size threshold st, which was chosen at the upper limit of the initial aerosol size distribution.
As shown in Figure 2, the deliquescence of sodium chloride can be clearly detected by an increase in aerosol size. This is measured as an increase in particle number concentrations above a size threshold \( S \), which was set at the upper limit of original aerosol size distributions. At -40°C, only deliquescence and homogeneous freezing near liquid water saturation was observable for INKA operation with a total flow rate of 12.5 l/min. Any ice crystals that might have formed prior to \( S_{liq} = 1 \) did not grow sufficiently to differentiate their light scattering signal from the non-activated aerosol.

At -50°C, the deliquescence is accompanied by a clear ice formation signal in the medium and upper channels of the OPC. Such simultaneous activation of heterogeneous freezing and deliquescence has also been observed in the AIDA cloud expansion chamber at the given temperature (Kaufmann, 2016). Reaching liquid water saturation, we detect homogenous ice nucleation as a further increase in total number concentration.

**CONCLUSIONS AND OUTLOOK**

When compared to extrapolated literature data on particle deliquescence (Tang and Munkelwitz, 1993), our data show reasonable agreement within the instrumental uncertainties. Also, homogenous ice nucleation of pure water was observed along the extrapolated liquid water saturation line. This demonstrates the operability of INKA and the validity of applied flow models in the cirrus cloud temperature regime.

The observed heterogeneous freezing behavior of sodium chloride aerosol below -50°C confirms findings from AIDA cloud expansion experiments. At warmer temperatures, heterogeneous freezing below liquid water saturation was not observed for the high aerosol flow rates used in this investigation. We will further investigate whether this is related to delayed ice crystal detection or to delayed equilibration rates in the experimental timeframe.

**ACKNOWLEDGEMENTS**

We thank Paul DeMott, Ezra Levin and Jens Nadolny for their help in the design and build up of INKA. In addition, we thank the whole AIDA team for the support during instrument development and measurements.

**REFERENCES**


Schiebel et al. (in preparation). A new continuous flow diffusion chamber INKA for ice nucleation measurements.

Characterization of individual ice nuclei by single droplet freezing method: A case study in the Asian dust outflow region

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Keywords: Ice nuclei, Mixed phase cloud, Mixing state.

INTRODUCTION

Ice nucleation in clouds substantially affects the climate by having a significant impact on the radiation balance and precipitation process in the Earth’s atmosphere. The super-cooled water droplets in the actual atmosphere generally form ice crystals at higher temperatures by the aid of aerosol particles that have the ability to nucleate ice than pure water. The physical and chemical properties of aerosols, which act as the ice nuclei, play an essential role in the formation of ice crystals. However, a considerable uncertainty still exists as to the response of IN processes to the changes in the hosting aerosol properties, due to the lack of fundamental understanding of the interaction of aerosol particles with the ice crystal formation.

Many previous IN experiments were performed under laboratory conditions and provided valuable knowledge on IN properties of pure component particles and artificially generated aerosol mixtures (Murray et al., 2012). However, the situation is even more complex in the ambient atmosphere, where particles are often present as a complex mixture of different compounds. Therefore, the necessity remained to conduct experiments that reflect the particle mixing state in the actual atmosphere. In particular, the reaction processes, coating and aging states at the surface of the particles can dramatically change from their original properties though internal mixing (Trochkin et al., 2003). It is often the case that internal mixing states can vary from particle to particle, therefore, individual particle analysis is necessary for establishing complete understanding of the ice nucleation by ambient aerosol particles.

This study is designed to investigate how morphology, chemical composition, and mixing state of ambient aerosol particles influence their ice nucleating activities under conditions relevant for the mixed phase clouds. We further demonstrate that we can also keep track on the individual ice nucleating particle by continuously controlling the ambient conditions during the ice nucleating experiment.

The individual droplet freezing method (IDF) is an experimental method used in this study, with which ice crystal formation on each particles under controlled condition can be monitored while maintaining individual particles distinguishable. We exposed the sampled particles to the conditions relevant for mixed phase cloud formation, thus simulating the ice nucleation at immersion freezing mode. By drying and evaporating the particles that formed ice crystals and/or droplets, further, one can keep track on their exact location as ice and/or droplet residues. This method enables detailed post sampling analysis on both ice forming and non-ice forming particles on individual particle basis. Here, we applied the method on ambient aerosols that were under the influence Asian dust outflow.

METHODS

The sample particles were deposited onto Si wafer substrate with hydrophobic coating. After particles were observed under an optical microscope (Fig.1a), the particles on the substrate were exposed to the water super saturation condition that initiates droplet formation by adjusting both the dew point of the air flow (0.5 l/min) introduced into cold stage cell (THMSG600, Linkam Scientific Instruments, UK) and the temperature of the sample on the cold stage (Fig. 1b). Then, the temperature of the stage was cooled down to -30 °C. The formation of ice crystals on individual droplets can be visually identified by the rapidly increasing size and their irregular shapes (Fig. 1c). After the substrate reached -30°C, the temperature of
the stage was increased up to -10°C. After reaching -10°C, the dry air flow (0.5 l/min) was introduced into the cell to expose the formed ice crystals and droplets to the sub-saturation condition for ice. As a result of evaporation and/or sublimation of water the nuclei particles were left visible on the substrate (Fig. 1d).

Fig. 1. Optical images of sampled particles on substrate before the ice experiment (a), exposed to the water super saturation condition at -9° C (b), cooled substrate at -30° C (c), and after the ice experiment (d).

By using the IDFM method, we identified the ice nucleating particles from the ambient aerosol particles. Five types of standard samples were also tested with the same method for comparison (Quartz, K-feldspar, Na-feldspar, Arizona test dust; ATD, Asian dust source particle; ADS). The ambient particles were sampled by using an impactor having a 50% cutoff diameter at 1.1 μm at a flow rate of 1.0 L/min at Kanazawa University campus (36.54°N, 136.70°E, 149 m. a. s. l.), Japan on 28 February 2016 and 10 April 2016. On both sampling days, arrivals of Asian dust plumes were reported.

Both IN active and non-active atmospheric particles identified by the IN experiments of the atmospheric particles were analyzed on individual particle basis using an atomic force microscope (AFM, CombiScope™ 1000, AIST-NT, Inc.) and a micro-Raman spectroscopy (Nanofinder™ HE, Tokyo Instruments, Inc.), for the characterization of 3 dimensional morphology and detection of surface chemical compounds under ambient conditions, respectively. Furthermore, the exact same particles were analyzed by a scanning electron microscope (SEM, S-3000N, HITACHI) coupled with an energy dispersive X-ray spectroscopy (EDX, EMAX-500, HORIBA), in order to obtain their elemental composition.

RESULTS

Fig. 2. Summary of the detection frequencies for the assigned components in the non-active, the IN active, and the Asian dust source (ADS) particles by micro-Raman analysis.

The heterogeneous IN by all standard samples tested in this study was always observed at higher temperatures than the homogeneous freezing temperature. The standard samples of single mineral components included pure water, K-feldspar, Na-feldspar and quartz, and their freezing onset temperatures were -36.5° C, -20.3° C, -20.7° C and -25.7° C, respectively. Therefore, the IN activity of K-feldspar was highest and that of quartz was lowest among these samples. The freezing temperatures of ATD and ADS particle were also found to be at -22.5° C and -26.6° C, respectively. Meanwhile, most of the IN active particles collected from the actual atmosphere formed ice below -28° C.

The morphological images and the maximum height based on the cross sectional shape of 22 IN active particles and 67 non-active particles were obtained by AFM observation on ambient samples. The results suggested that the IN active particles were predominantly irregular particles.
Chemical species contained in the 42 IN active particles and 131 non-active particles were identified by the Raman spectra (Fig. 2). The significantly larger fraction (76%) of the IN active particles showed fluorescence in the Raman spectra. In addition to the fraction of fluorescent particles, BBC such as humic like substances or black carbon, CaSO₄, and quartz were detected in the IN active particles with obviously higher frequencies than the non-active particles.

Elemental compositions of 37 IN active particles and 114 non-active particles were analyzed by using SEM-EDX. As shown in Fig. 3, the relative abundance of particle groups were clearly different between the IN active and non-active particles. The mineral dust particle groups (mineral dust and mineral dust + inclusions) accounted for 55% of the IN active particles and were the most dominant types. On the other hand, the majority (62%) of the non-active particles was dominated by the fresh and aged sea salt particles. In the Ca-rich and sulfate groups, their pure component groups were relatively larger as compared to their internal mixtures (+ inclusion) among the non-active particles.

Fig. 3. Frequencies of the identified particle groups by SEM-EDX for the non-active and the IN active particles during April and February sampling.

DISCUSSIONS

Based on the results of SEM-EDX and micro-Raman analysis, most of sea salt particles can be considered as the aged sea salts particles that were internally mixed with nitrates (in particular MgNO₃), sulfates or organics. As a result of the current freezing experiment, it was clearly demonstrated that these aged sea salt particles are not efficient ice nuclei in the mixed phase cloud formation. We show ternary diagram of Na-(Al+Mg+Fe)-(Ca+S) for all analyzed particle in (Fig. 4). The diagram clearly indicates that particles having Na larger than 35% were predominant in the non-active particles. That is an indication that internal mixing with sea salt particle may potentially act as an important inhibiting factor for the IN within the mixed phase clouds.

The fluorescent particles identified by micro-Raman can be associated with mineral dust (especially those enriched in clay minerals) from the comparison with the SEM-EDX analysis. Therefore, both the SEM-EDX and micro-Raman analyses suggested that mineral dust particles act as efficient ice nuclei under conditions relevant for the mixed phase cloud formation in the atmosphere.

Additionally, In order to verify the importance of mineralogy (e.g. whether K-feldspar is dominant within the ice nucleating particles), the particle group identified as mineral dust were further classified based on the ratio of the detected elements. It turns out that, K-feldspar dominant particles were hardly observed in the atmospheric mineral dust particles analyzed in this study. Also, the peaks of feldspar and quartz were hardly identified in the Raman spectra of the analyzed mineral dust particles. Further, the standard K-feldspar and quartz samples were indeed much more efficient IN than atmospheric IN active particles. The above results suggested that ice nucleating mineral dust particles as efficient as pure component K-feldspar or quartz are extremely rare in the actual atmosphere. On the other hand, it was demonstrated that most of the ice nucleating particles above -30°C in the atmosphere were dominated by mineral dust particles composed mainly of clay, with or without minor mixing of other mineral
components, that involves fluorescence most likely as a result of the defects and/or impurities such as humic organics in their clay minerals (Gaft et al., 2005; Sovanska et al., 2014).

In terms of Ca-rich particles classified by SEM-EDX, those particles with small S content (S/Ca<0.2) that can be regarded as predominantly calcite were more common in the non-active particles. The 50% of the analyzed those Ca-rich particles were detected with the peak of carbonates in the Raman spectra, confirming the presence of calcite in the non-active particles. In the case of sulfate particles, the non-active sulfate particles showed peak of (NH₄)₂SO₄. In contrast, the particles identified as CaSO₄ and fluorescence peak were clearly showed relatively higher abundance within the IN active sulfate particles. With regard to the Ca-rich and sulfates particles studied, in summary, our results show evidence that the (NH₄)₂SO₄ or intact calcite particles in the actual atmosphere were suggested to be inactive IN under mixed phase cloud formation. Meanwhile, CaSO₄ or the particles internally mixed with minor fraction of clay mineral or sulfates particles may have higher chance of nucleating ice than the (NH₄)₂SO₄ or intact calcite particles.

With all above results considered, it is suggested that, in addition to the original composition and related IN activities, the aging process in the atmosphere must also be taken into account for precisely predicting the IN activity of the ambient aerosols.

CONCLUSIONS

The IN experiments on both the standard mineral samples and the ambient aerosol particles were performed on individual particle basis by the IDFM. In addition, morphology and composition of both the IN active and non-active particles were directly measured by three different individual particles analysis.

Among the ambient aerosol particles, alumino-silicate mineral dust and internal mixtures particles in sulfates or Ca-rich particles were identified as ice nucleation active particle types. The mineral dust were suggested to be clay mineral or mixtures of several mineral components rather than single mineral species that were previously associated with high ice nucleation activity (e.g. K-feldspar). Our result suggests that the freezing temperatures of individual IN in the actual atmosphere do not show large variation and fall in the relatively narrow range that can be represented by ice nucleation activity of clay minerals.

On the other hand, the aged sea salts, pure calcite, and pure sulfates were found less active as IN. Especially, the mixing with sea salt particles during transport is suggested as an important factor inhibiting the IN activity of the mixing counterparts (e.g. mineral dust). Although pure calcite and sulfate particles were identified as inert particle groups, interestingly, their internal mixture showed relatively higher IN activity. This may have an important implication such that the atmospheric aging (including cloud processing) could potentially enhance the originally inert IN activity of calcite or (NH₄)₂SO₄ particles.

This study successfully related the immersion-mode IN activity of atmospheric particles and their morphology, composition and mixing states on individual particle basis. This was made possible by the direct and comprehensive particle analysis on the individual ice residue particles. We believe the method can be used to verify the aerosol IN theories previously proposed mostly based on experiments using single component and/or bulk samples.

REFERENCES


ICE NUCLEATION ACTIVITY OF ARABLE SOIL DUST AEROSOL PARTICLES


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Keywords: ICE NUCLEATION, SOIL ORGANIC MATTER, CLOUD FORMATION.

INTRODUCTION

Only a minor fraction of atmospheric aerosol particles acts as a trigger for heterogeneous ice formation in clouds. Nevertheless, the activity of these ice nucleating particles (INPs) controls primary ice formation, which may be followed by secondary ice multiplication processes, and thereby markedly influences cloud radiative properties as well as the initiation of precipitation. Soil mineral dust aerosol INPs, mostly from deserts, are widely acknowledged to be important for ice formation in clouds. On the other hand, recent investigations have shown that agricultural soil dust has an enhanced ice nucleation activity of up to a factor of 10 compared to desert dust, especially at temperatures above -26°C (Steinke et al., 2016). This enhancement appears to be caused by very ice-active primary biological particles, such as bacteria, fungal spores and pollen, and their cell-free INP proteins and other macromolecules (Hoose and Möhler, 2012; Fröhlich-Nowoisky et al., 2012; Pummer et al., 2015). Compared to desert dust particles, arable soil dust aerosol also contains a considerably higher amount of organic matter, derived from plants and the soil microflora, which further increases its ice nucleation activity (O’Sullivan et al., 2014; Tobo et al., 2014; Hill et al., 2016).

To be able to assess the influence of arable soil dust aerosol on natural cloud formation, there is a need for more quantified information on its ice nucleation behavior and its origin. We present comprehensive laboratory investigations which aim to fundamentally understand and quantify the contribution of soil organics to aerosol ice nucleation activity.

LABORATORY INVESTIGATION ON THE ICE NUCLEATION ABILITY OF ARABLE SOIL DUST AEROSOL

To investigate the ice nucleation activity of soil dust, we conducted a series of laboratory measurements in the cloud simulation chamber AIDA (Aerosol Interactions and Dynamics in the
Atmosphere) with five different soil dust samples from Argentina, Germany and Wyoming. All samples were collected from topsoil. The samples were dried and sieved, before their dispersion and injection as aerosol into the AIDA chamber. There, the aerosol was characterized by a CPC (condensation particle counter), SMPS (scanning mobility particle sizer) and an APS (aerodynamic particle sizer). In addition, the chemical composition of the aerosol was analyzed by the single particle mass spectrometer LAAPTOF (Laser Ablation Aerosol Particle Time-of-Flight Mass Spectrometer, Aeromegt GmbH). To measure the ice nucleation activity of the samples, four different INP measurement techniques have been used, all sampling or collecting particles from the same aerosol source.

The AIDA chamber operates under atmospherically relevant conditions over wide ranges of temperature, pressure and humidity. By controlled adiabatic expansions, the ascent of an air parcel in the troposphere was simulated. The forming ice particles were detected in order to investigate the ice nucleation activity of the aerosol particles. In addition, the continuous flow diffusion chamber (CFDC) INKA was used for this study. Here, the sampled aerosol is exposed to a defined temperature and saturation ratio in order to investigate its ice nucleation activity under these pre-set conditions. Further, we collected aerosol particles from the AIDA chamber for two INP offline measurement techniques CSU-IS (Colorado State University Ice Spectrometer) and MINA (Mono

Figure 1: AIDA data time series of two experiments started at -17°C. This figure shows the decreasing pressure and temperature (panel 1), the increasing relative humidity (panel 2) and the ice particle number concentration (panel 3) in the course of the experiment. The ice nucleation activity of the soil dust aerosol sample (blue) is strongly reduced due to heat treatment (2 h at 300°C, red).
Ice Nucleation Assay). For both of these immersion freezing methods, ultra pure water was used to wash off the collected particles from the filters, and then the ice nucleation activity of small aliquots of this suspension was investigated. For organic matter pyrolysis, we heated the samples at 300°C for two hours. By investigating the difference in activity of the untreated and the heat treated sample we could assess the importance of the organic matter to the ice nucleation activity of arable soil dust. The AIDA results show that the ice nucleation activity was significantly reduced by the heat treatment (Fig. 1). In addition, we heated the CSU-IS aerosol suspension to 95°C prior to re-analysis in order to denature more heat labile compounds and proteinaceous INPs.

CONCLUSIONS

The combination of results from four different INP measurement techniques provides a robust data set on the ice nucleation activity of arable soil dust aerosol over a wide temperature range in the immersion freezing regime. Due to denaturation of proteinaceous particles and pyrolysis of organic compounds, the contribution of these components to the ice nucleation activity of arable soil dust particles was investigated.

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REFERENCES


NOVELTIES IN ICE NUCLEATION TERMINOLOGY

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Keywords: HETEROGENEOUS ICE NUCLEATION, TERMINOLOGY.

INTRODUCTION

A revision of the Nucleation Terminology of 1985 was put forth in Atmospheric Chemistry and Physics (15, 10263, 2015; VDMW15), focused on ice nucleation. For some of the terms dealt with in VDMW15, in connection with heterogeneous ice nucleation, additional explanations are offered here with a grouping by the degree of novelty involved. The goal is to promote the acceptance of the terms and to motivate discussion about the principles involved.

MOST NOVEL, MOST CONTROVERSIAL

1. Site nucleation rate (4.7.2)¹. This term is suggested as a clear indication for the probability of nucleation on a site of given characteristics. In principle this is the most fundamental measure for heterogeneous nucleation. This is the quantity that is derived from CNT² where the physical parameters defining the site are specified.

Site nucleation rate has been given the symbol \( J_{\text{site}} \), but it is the same as designated as \( J_{\text{Tc}} \) in Vali (2008). Empirically, different sites are diagnosed by their freezing temperatures and this temperature can be taken as being a first estimate of the characteristic temperature of the site (in terms of the VS66 model); hence the equivalence of \( J_{\text{site}} \) and \( J_{\text{Tc}} \).

What is new with this definition is the focus on site-specific nucleation, i.e. recognizing that the value derived from CNT, or determined from experiment, is specific to a sub-set of potential sites in a sample. The emphasis on site-specificity is necessary in order to distinguish it from nucleation rate in homogeneous nucleation, and from the assumed cases of infinite number of sites of identical potential for nucleation under given conditions. Here, we stress that the fact that when a large spread of freezing temperatures, say more than 5°C, is observed in an experiment, that spread can safely be assumed to be due to difference in effectiveness of sites and not a statistical spread associated with a single value of the rate coefficient. The 5°C spread is quite conservative, as current evidence points to an even smaller value, more like 1-2°C (Vali 2008; Wright and Petters et al. 2013). These estimates are inferred from repeated observations of the freezing temperatures of the same drop, which is dilute enough.

¹These numbers refer to the paragraph on the topic in VDMW15
²The symbols and acronyms given in VDMW15 are used in this communication. They are listed in Table 1 of VFMW15.
to minimize the probability of containing more than one INP and more than one site. A narrow range of freezing temperatures for a population of drops (such as reported in Wex et al. 2015) may also arise with high numbers of INPs that carry identical sites so a site nucleation rate may also be inferred from that data. However, the proof for the identical configuration of sites, or for the lack of alteration of single sites in repeated freezing tests, should, ideally, have independent confirmation. Such independent confirmation is not feasible with current methods, so inferences for \( J_{site} \) from either method are the best estimates that can be obtained.

2. **Stochastic description (4.8.1).** The main novelty, or clarification in this case, is to emphasize that the stochastic description means assuming that there are a very large number of locations (sites) on the surface of the nucleating material with the same probability of having a critical embryo form on it. When freezing temperatures in an experiment are observed to extend over a range \( \Delta T \) and the results are assumed to arise from a single nucleation rate function \( J \), it follows that the range of appreciable values of \( J \) also extend over the same \( \Delta T \). For \( \Delta T \) greater than 1-2°C, this contradicts the expectation from homogeneous nucleation and from relevant experiments (not detailed here) that the \( J \) function is a very steep function of temperature. In a number of papers the data are reconciled with theory on the basis of multiple \( J \) functions representing a variety in nucleating ability (cf. Section 4.8.2 in VDMW15)

3. **Freezing rate (4.6).** (Some authors use "extensive nucleation rate" for the same concept.) This term is a straightforward representation of the results of freezing experiments with multiple sample units. The distinction between freezing rate, \( R \), and nucleation rate \( J \), is worth emphasizing since assuming the two to be the same implies the acceptance of a stochastic description, and in many papers is then identified as an application of CNT. However, use of the first order reaction equation \( rate = \frac{1}{N}(\delta N/\delta T) \) to describe the rate at which freezing is observed for number of sample units is, strictly speaking the freezing rate \( R(T) \). Interpretation of this rate as the nucleation rate \( J(T) \) is only valid (as in homogeneous nucleation) if all sample units are identical. For heterogeneous nucleation that can only be satisfied if the INP content of all sample units is exactly the same, with the same surface characteristics. This condition is very demanding and in view of the complexities of surfaces can’t be fulfilled with simple measures of laboratory procedures. Neither is there any simple inference from the observations of \( rate \) that the condition of uniformity is fulfilled or not. Thus, using \( rate = J(T) \) and then using CNT to interpret the observations is very difficult to justify.

IN WIDESPREAD USE

1. **INP – ice nucleating particle, and its variants like INM (4.1).** The main change with this term is to replace the use of ice nucleus, IN, in order to recognize that the reference is in the vast majority of cases is, in fact, to the particle that carries the ice nucleating site, not to the embryo which is really the ice nucleus. Variants of the term, such as INM has also seen fairly extensive use to refer to ice nucleating macromolecules. In that case too, the site is a minor part of the entity, so referring to as INM is more informative.

2. **Modes of hetrogenous ice nucleation (4.4).** Reference to "modes" to distinguish between freezing and deposition nucleation has been well established in the literature. What is somewhat new in comparison with the 1985 definitions is the lack of emphasis on condensation-freezing and a much reduced focus on contact nucleation. This is due to the lack of clear evidence that these pathways are fundamentally different from immersion freezing. Both are freezing events initiated by an INP within supercooled water. Freezing within pores appears
to be consistent with observations that were previously interpreted as deposition (Marcolli 2014).

OUTSTANDING

Entries in this list represent newer, less settled or less known designations and concepts. Publications of recent years reveal that there are many important questions concerning these processes, which, by turn, are also of potential relevance to the processes believed to be better understood.

1. Contact nucleation (4.4.2). Also called, although with subtle differences surface nucleation or edge nucleation. Literature support is fairly strong, though not extensive, for preferential nucleation with the ice nucleating surface, INS, when located at the outer boundary of a water drop, i.e. at the water-air-INS interface. This situation may arise, to take an atmospheric example, as a result of a collision between an INP and a water drop. In the laboratory, a variety of arrangements has been used to create the water-air-INS interface (e.g. Ladino et al. 2013; Niehaus et al. 2014; Gurganus et al. 2014; Yang et al. 2015; Nagare et al. 2016). It isn’t yet clear if a distinction needs to be made between the cases in which the drops are supercooled at the moment of collision and cases in which the particle remains at the surface following collision at some earlier time (termed "adhesion freezing" in Nagare et al. 2016). A difference has been reported depending on the INP being located inside or outside the drop, i.e. mostly in the liquid or mostly in the air. The dynamic effect of a collision, or the preconditioning of the INP prior to collision are other potential sources for influencing the outcome. Further clarification will have to be awaited to narrow the evidence on these modes of ice nucleation. These processes may have practical impacts, specially in cloud glaciation, and are intriguing processes whose clarification can provide important insights to nucleation.

2. Dynamic effects. A moving water-substrate interface has long been associated with freezing on shaking and other similar phenomena. Few reproducible and quantitative experiments have been performed, so that knowledge of these dynamic effects in not much beyond anecdotal. Movement associated with electrowetting has been shown to lead to enhanced nucleation in Yang et al. 2015. As mentioned in the previous paragraph, contact nucleation may also involve a dynamic effect.

CONCLUSIONS

The study of ice nucleation is progressing at a rapid pace. This is clearly reflected in the state of flux that is evident in the nomenclature of heterogeneous ice nucleation. Many concepts are being reviewed, revised and brought into question by new evidence. All this puts special demands on communicating ideas and describing results carefully and unambiguously. Any set of definitions – terminology – will undergo both gradual acceptance and continuous revision. This paper is just a marker in that process.

REFERENCES


LABORATORY STUDIES OF IMMERSION MODE HETEROGENEOUS ICE NUCLEATION

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Keywords: LABORATORY EXPERIMENTS, ICE NUCLEATION, IMMERSION MODE, AQUEOUS SOLUTION.

INTRODUCTION

Aerosols affect the climate system not only by changing the opacity of the air, but also due to the formation of water droplets and ice crystals in the clouds (Sadykova et al., 2014). Ice crystals play a significant role in the formation of radiation properties of clouds and precipitation processes. To build a model of the phase state of the clouds we carried out laboratory experiments on immersion mode heterogeneous ice nucleation in aqueous solutions.

METHODS

The experimental setup LINC for investigation of the ice nucleation was created in Laboratory of Meteotehnology, RSHU (Nikulin et al., 2015). The experimental installation consists of an optical microscope, digital microscope, temperature sensors, freezer and Peltier module. The optical microscope is used for the preparation of substrates and drops. The temperature of Peltier module is controlled by a programmable power supply. The images of freezing droplets are obtained with the help of the digital microscope. Moment of droplet freezing is determined automatically by computer vision system. The experimental installation allow one to carry out experiments at 243 K and below.

The particles of kaolin and quartz were used in laboratory experiments. According to the experience, the surface area of the substrate plays an important role in the ice nucleation. The substrate properties of ice nuclei formation are described by the parameter, named specific linear energy (SLE) (Chukin and Platonova, 2009). In the theory of ice nucleation by Chukin-Platonova this parameter characterizes the properties of substrates: the less SLE, the easier the formation of ice crystals on a substrate.

DATA AND ANALYSIS

The amount of experiments on the crystallization of supercooled droplets of aqueous solution with the water activity in range from 0.97 to 1.00 equals 359. Example comparison of the experimental data and the model is shown in Figure 1. Analysis of the experimental data showed that the average values of the SLE of kaolin and quartz particles are 16.1 ± 1.8 and 17.8 ± 0.9 pJ/m, respectively. The temperature dependence of SLE was found. It can be approximated by the equations

\[
SLE_{\text{kaolin}} = 1.379 \times 10^{-10} - 4.782 \times 10^{-13}T, \tag{1}
\]

\[
SLE_{\text{quartz}} = 1.134 \times 10^{-10} - 3.821 \times 10^{-13}T. \tag{2}
\]
CONCLUSIONS

The phase state of cloud can be determined on the basis of the obtained results as a function of temperature and concentration of aerosols. This will not only allow to simulate the effect of aerosols on the radiative properties of clouds, but also to determine the crystallizing properties of the aerosols from satellite data.

REFERENCES


ESTIMATION OF THE CO$_2$-INDUCED TERRESTRIAL CLIMATE FEEDBACK IN SUBARCTIC REGION

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Keywords: Feedback loop, aerosol-cloud interactions, gross primary production, aerosol formation and growth

INTRODUCTION

The atmosphere forms suitable circumstances for living on Earth. In the chaotic atmosphere, every deflection from the normal conditions can have an unexpected effect on fragile interactions. Due to anthropogenic emissions, concentrations of greenhouse gases have increased significantly during last century, constituting the most important forcing term in the global warming (IPCC, 2013). Although the rate of changes of greenhouse gas concentrations are well known, the impacts of these changes are not straightforward as the internal variability of the atmosphere and climate is not fully understood. Most important causes for uncertainties are radiative forcing of aerosols and aerosol-cloud interactions, as well as various feedback loops in the climate system that can amplify or dampen the original forcing.

The continental biosphere has a major role in the climate system, as it effects on the amounts of carbon dioxide and other greenhouse gases in the atmosphere (Heimann and Reichstein, 2008; Ballantyne et al., 2012), in addition to which it is a source of natural aerosols (Pöschl, 2005; Guenther et al., 2012). Kulmala et al. (2004) suggested that higher temperatures and CO$_2$-levels would enhance the continental biomass production, and thereby lead to increases in biogenic secondary organic aerosol (BSOA) and cloud condensation nuclei (CCN) concentrations, which tend act to cool the atmosphere. Kulmala et al. (2013) extended the continental biosphere-aerosol-cloud-climate (COBACC) feedback mechanism by a connection between aerosol particles, radiation and gross primary production (GPP) – a measure of the ecosystem-scale photosynthesis. Finally, Kulmala et al. (2014) provided an estimate of the strength of the feedback loop connecting GPP, associated with the carbon uptake, organic aerosol formation in the atmosphere, and transfer of both diffuse and global radiation. Their analysis was based on long-term field measurement data set collected from a boreal forest site in southern Finland.

We investigated whether a feedback mechanism similar to that described above can be identified from a measurement site in Eastern Lapland in Finland. The measurement site differs from the previous one. In Lapland, the measurement site is located on a top of a hill 390 m above the sea level and 250 km north of the Arctic Circle. The location in high latitudes causes the forest to be more stunted than it is in southern Finland. Although the main species is 60-year-old Scots pine (Pinus Sylvestris L.), the mean tree height and diameter are approximately only eight meters and eight centimeters. The station has no local sources of pollutants, and most of the time the air is pollution free. Occasionally, the air is polluted by the air advected from the Nikel and Montschegorsk smelters less than 200 km north and east of the station, respectively. These differences have an effect on the connections of the feedback loop as the circumstances for the interactions are different. The aim of this study was to find out whether the above-mentioned feedback mechanism exists in the subarctic region, and to make a preliminary estimate on the strength of this feedback.
Figure 1. The part of the COBACC feedback loop that is going to be investigated. The four steps can be examined separately. GPP refers to the gross-primary production, GR$_{org}$ is the particle growth rate caused by organic vapor condensation, CS address to condensation sink, and R is the ratio between diffuse and direct photosynthetically active radiation (PAR) (Kulmala et al., 2014).

METHODS

To estimate the existence and strength of the overall feedback loop, it was divided into four subsequent steps by selecting four key quantities similar to Kulmala et al. (2014). Figure 1 illustrates the steps and the quantities that are gross primary production (GPP), particle growth rate due to organic vapor condensation (GR$_{org}$), condensation sink (CS), and the ratio between the diffuse and direct photosynthetically active radiation (R). GR$_{org}$ is used as it is a good proxy for the gas-phase concentration of low-volatile vapors resulting from atmospheric BVOC oxidation (Kulmala et al., 1998; Paasonen et al., 2010). The condensation sink is a measure of the amount of biogenic secondary organic aerosol as it describes the ability of the pre-existing aerosol particle population to remove condensable vapor molecules from air, in addition to which it is a relatively good proxy to the aerosol light scattering coefficient (Virkkula et al., 2011). Higher values of R tend to advance photosynthesis and GPP (Mercado et al., 2009). Thus, the increased aerosol load and R increase GPP (e.g. Anton et al., 2012), leading to the final step of the introduced feedback mechanism.

The strength of the individual steps will be estimated from long-term measurement data provided from the measurement site located in subarctic forest in Finnish Lapland, to finally solve the strength of the whole loop as Kulmala et al. (2014) suggested.

OUTLOOK

To obtain enough data, comprehensive continuous observations are needed. The strength of the individual steps will be estimated from long-term measurement data provided from the measurement site located in subarctic forest in Finnish Lapland, to finally solve the strength of the whole loop as Kulmala et al. (2014) suggested.

ACKNOWLEDGEMENTS

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REFERENCES


IN-SITU CLOUD MEASUREMENTS DURING THREE PALLAS CLOUD EXPERIMENTS

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Keywords: clouds, Pallas, in-situ, probes

INTRODUCTION

Clouds properties and their formation are poorly understood in the global climate system and the aerosol effect via clouds forms the largest source of uncertainty in predictions of climate change (IPCC, 2013). Many of the climatically important cloud properties (e.g. albedo, precipitation rate and lifetime) depend, amongst other factors, on the number concentration of aerosol particles and on their chemical composition (Komppula et al., 2005; Lihavainen et al., 2008).

Continuous, semi-long term, ground based, in-situ cloud measurements were conducted during the autumn intensive Pallas Cloud Experiments (PaCE) in years 2012, 2013 and 2015. The main motivation for those campaigns was to investigate aerosol cloud interaction. The measurements were conducted in Finnish sub-Arctic region at Sammaltunturi station, the part of Pallas-Sodankyla- Global Atmosphere Watch (GAW) programme.

METHODS

The Sammaltunturi measurement site (67°58’N, 24°07’E, 560 m a.s.l.) is located at a hill top. During autumn, the station is usually about 50% of the time inside a cloud which allows direct in-situ cloud measurements. During PaCE 2012, 2013 and 2015 the Cloud, Aerosol and Precipitation Spectrometer probe (CAPS., DMT) (0.51 μm– 930 μm) and the Forward Scattering Spectrometer Probe (FSSP-100, DMT) (1.2 - 47 μm) were installed at the roof of the station (Fig.1). The CAPS probe includes two instruments for droplet size measurements: the Cloud and Aerosol Spectrometer (CAS) (0.51 μm - 50 μm), and the Cloud Imaging Probe (CIP) (12.5 μm – 930 μm). In this abstract we provide only result examples from the analysis of the cloud properties and how they were influenced by meteorology made only for CAS measurements.

Figure 1. A) FSSP-100 and B) CAPS probes as they were installed on Sammaltunturi measurement site during PaCE 2015.

In this work in order to estimate the presence of a cloud at the measurement site we used the cloud droplet count measured with the cloud probes. This was then crosschecked against the visibility measurements. We considered that the station was inside a cloud while the horizontal visibility was less than 1000 meters.
RESULTS

Example statistical information about Pallas experiments are summarized in Table 1. PaCE 2012 lasted from September 13th till October 30th, PaCE2013 lasted from September 14th till November 28th and PaCE 2015 lasted from October 6th till December 2nd. CAPS measurements covered around 90% of each campaign. However during PaCE 2013 the coverage was less because during the first month of the campaign, CAPS was not installed due to service maintenance delays. As a cloud event we defined the situation when the station was inside a cloud for at least a part of the day. Half an hour of continuously cloud measurements was set as the minimum limit of a cloud event. All the meteorological data which are demonstrated in Table 1 were calculated only for the period that the station was inside a cloud.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Days of the campaign</th>
<th>Cloud event days</th>
<th>CAPS coverage</th>
<th>temperature range (C°)</th>
<th>wind speed avg (m/s)</th>
<th>visibility avg (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PaCE 2012</td>
<td>48</td>
<td>40</td>
<td>90%</td>
<td>from -9.5 to 6.6</td>
<td>6.5 (2.4)</td>
<td>301.4 (179.9)</td>
</tr>
<tr>
<td>PaCE 2013</td>
<td>75</td>
<td>64</td>
<td>44%</td>
<td>from -12.0 to 9.9</td>
<td>7.3 (2.8)</td>
<td>338.3 (202.1)</td>
</tr>
<tr>
<td>PaCE 2015</td>
<td>59</td>
<td>34</td>
<td>88%</td>
<td>from -7.0 to 4.7</td>
<td>6.85 (2.4)</td>
<td>382.8 (210.4)</td>
</tr>
</tbody>
</table>

Table 1: General information about the PaCE 2012, 2013 and 2015. Table shows total number of days, number of days with cloud events, CAPS coverage (%) during cloud events, the temperature range (°C) when the station was inside a cloud and the average wind speed (m/s) and visibility (m) along with corresponding standard deviations (in brackets) when the station was inside a cloud for each campaign.

In Table 2 the averaged data for effective diameter (ED_{CAS}), median volume diameter (MVD_{CAS}) and liquid water content derived from CAS size distribution (LWC_{CAS}) during all three campaigns are also summarized.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>ED_{CAS} (um)</th>
<th>MVD_{CAS} (um)</th>
<th>LWC_{CAS} (g/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PaCE 2012</td>
<td>14.10 (5.21)</td>
<td>15.39 (5.46)</td>
<td>0.040 (0.032)</td>
</tr>
<tr>
<td>PaCE 2013</td>
<td>13.38 (2.35)</td>
<td>14.86 (4.25)</td>
<td>0.025 (0.020)</td>
</tr>
<tr>
<td>PaCE 2015</td>
<td>12.28 (5.10)</td>
<td>13.38 (5.38)</td>
<td>0.029 (0.027)</td>
</tr>
</tbody>
</table>

Table 2: Averaged data of ED_{CAS}, MVD_{CAS} and LWC_{CAS} along with corresponding standard deviations (in brackets) when the station was inside a cloud for all three campaigns.

Figure 2 indicates the averaged values along with standard deviations of the ED_{CAS}, MVD_{CAS} and LWC_{CAS} for each campaign. Effective diameter (upper left), liquid water content (upper right) and median volume diameter (lower left) show that the averaged values during each campaign were similar. In addition the temperature trends and temperature range (lower right) were also similar for each year of the campaigns.
Figure 2. Horizontal lines represent the length of each campaign (PaCE 2012, 2013 and 2015) and averaged effective diameter, liquid water content and median volume diameter along with standard deviation. The daily averaged data for the temperature versus time for each campaign is also presented.

ACKNOWLEDGEMENTS

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REFERENCES


POSSIBILITIES AND CHALLENGES OF USING SATELLITE DATA FOR ESTIMATING SULPHURIC ACID CONCENTRATIONS

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Keywords: Satellite remote sensing, Ozone Monitoring Instrument, sulphuric acid, proxies.

INTRODUCTION

Sulphuric acid act as a major contributor to new particle formation and the subsequent growth of the freshly formed particles (e.g. Kulmala et al., 2004, Sipilä et al., 2010). However, sulphuric acid measurements are challenging to carry out and therefore the availability of observations is rather limited. To overcome this issue proxies have been developed, where sulphuric acid concentrations have been estimated by combining in situ measurements of SO2 concentrations, radiation and aerosols, i.e. parameters that have been shown to be connected with sulphuric acid concentrations (Petäjä et al., 2009, Mikkonen et al., 2010). The aim of this work is to investigate the possibilities to use satellite data for the proxies to estimate sulphuric acid concentrations. We use observations from the Dutch-Finnish- built Ozone Monitoring Instrument (OMI), onboard NASA’s Aura satellite. The advantage of using OMI data is that, in addition to global coverage, SO2, aerosol, and UV-radiation observations are all available from the same satellite instrument.

DATA AND METHODS

The OMI instrument has been monitoring key air quality components including O3, NO2, SO2 and aerosols, as well as UV-radiation since 2004. In this work we will use the OMI Level 2 daily data of SO2 (planetary boundary layer product, PBL), UV radiation, and aerosol optical depth (AOD), gridded into a global 0.25x0.25° grid. Different combinations of the satellite-based parameters will be tested for the proxies, and the results will be compared with in situ data. Figure 1 shows an example of the yearly median of OMI SO2 over China, as well as the median of one possible satellite-based proxy, where the sulphuric acid “source” term SO2:UV has been divided by AOD, i.e. the “sink” due to ambient aerosols.

![Figure 1](image_url)  
*Figure 1. Yearly median (2013) of OMI SO2 (left) and OMI SO2:UV divided by OMI AOD (right), a potential satellite-based proxy for sulphuric acid.*
REFERENCES
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3. Li-Hao Young: Performance evaluation of a VTDMA-APM system for the volatility and effective density of ultrafine particles

4. Katherine Nadler: Temperature dependent spectroscopy of single model sea spray aerosol

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18. Marzieh Khansari: Studying aerosol radiation feedback loop based on satellite data

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23. Qiaozhi Zha: Measurement of HOMs at two different heights: influence of planetary boundary layer on HOM chemistry

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53. Michel Attoui: Design and calibration of 1nm butanol CPC

54. Juha Kangashuoma: Electrospray generation of singly charged sub-4 nm clusters

55. Tiia Laurila: Improved counting statistics of an ultrafine DMPS system by utilizing ultrafine A20 CPC with optics flow rate of 2.5 lpm
PROBING STRUCTURE AND CHEMICAL PROPERTIES OF FREESTANDING CLUSTERS WITH SYNCHROTRON RADIATION. PART II: AQUEOUS SALT CLUSTERS AND ATMOSPHERIC APPLICATIONS.

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Keywords: Aqueous salt nanoclusters, surface structure, atmospheric composition.

INTRODUCTION

In PART I of this abstract, we present our custom-built Exchange Metal Cluster (EXMEC) and new Multiuse Setup for Clusters Emission (MUSCLE) setups for production of neutral, multiple-component clusters with a wide range of compositions, sizes, and structural properties. Each cluster source can be combined with highly surface sensitive synchrotron radiation (SR) based photoelectron spectroscopy (PES) for direct and specific probing of target elements and their chemical environment, while resolving contributions from the cluster surface and bulk phases. This provides a complementary method to e.g. ion mass spectrometry, allowing us to probe detailed chemical and structural properties of nanoclusters decoupled from their method of production. The range of applicability of PES to continually renewed low-density samples is greatly enhanced by the brightness of the new MAX IV synchrotron light source. Here, we emphasize features of this experimental setup of particular interest to the study of atmospherically relevant nanoscale systems.

METHODS

As a starting point, clusters are produced neutral and can subsequently be charged in a controlled manner, if required for analysis. The charge state of molecular and nanoscale clusters may impact their properties and characterization, as well as their role in atmospheric new particle formation, in ways which may still not be well understood (Kulmala et al., 2014). This feature is therefore highly advantageous for detailed mechanistic experimental studies of clusters representative of those involved in such events.

Atmospheric samples, such as in particular organic aerosols, are insulators. Using PES, the probing synchrotron radiation therefore immediately charges the material in a static bulk sample, but due to the continual rapid renewal of the sample in the beam of freestanding clusters, spectral artifacts from such charge effects are largely avoided. In addition, this rapid renewal of the cluster beam allows us to use X-ray and other PES techniques for studying complex mixtures of volatile and semi-volatile atmospheric organics, which as static samples would respond very differently to the evaporative driver as they are introduced to the continuously evacuated low pressure interaction region to intersect the SR photons. Furthermore, producing the low density cluster beam requires only very small amounts of sample material, which is advantageous for the – at times – immensely sparse atmospheric samples.

Sizes of the clusters produced currently range from a few to several hundreds and in principle thousands of entities (single atoms, molecules, salt formula units). For example, in the case of inorganic salts, we have produced clusters with diameters up to about 5 nm (Hautala et al., 2014;
Cluster size and size distributions can be controlled in several ways, primarily by varying the different target gas pressures or the temperature and shape (inner hole diameter) of the nozzle. For the adiabatic expansion part, lower nozzle temperatures in general yield larger clusters. In the exchange region, the vapor pickup cross section depends almost exclusively on host cluster size, but extending the pickup region can allow for longer exchange times and greater pickup as well. Currently, the upper size limit of clusters produced by exchange is strongly substance dependent, mainly modulated by the target dopant vapor pressure, as determined by the saturation vapor pressure, evaporator temperature, and the volume of the pickup region. There is no lower limit on cluster size produced with this method: beyond monomers, anything from dimers and trimers are accessible, allowing us to study detailed molecular level properties of clusters representing even the earliest stages of nucleation and new particle formation, e.g. in the atmosphere.

In principle, clusters of any composition (components and mixing state) can be produced, limited only by our ability to transfer the individual substances to the vapor phase intact. This may be highly relevant for atmospheric systems, where the ubiquitous occurrence of phase separation in clusters and aerosols is now becoming evident. To study detailed properties of such systems, we must be able to produce clusters with compositions spanning a wide range of (meta-)stable mixing states. By using a separate evaporation section for each substance, we are able to mix components with a wide range of vapor pressures, in particular water, inorganic salts, metals, and a suite of atmospheric organics. The composition of clusters with several components can be varied independently of e.g. mutual miscibility of the different components in the liquid phase. With only a single evaporation section, control of cluster composition is greatly limited outside the special cases of azeotropic mixtures (where liquid and gas phases have identical molar composition), reducing the range of accessible overall mixing states for the clusters. Furthermore, we can target cluster morphology and even phase state, e.g. crystal structure, solid-solid radial composition profiles, and liquid-liquid phase separation. For example, by placing the different evaporation sections in either series or parallel, we can allow for either homogeneous mixing or spatially segregated composition profiles.

PES using synchrotron radiation allows us to probe element and compound specific composition and local environment with very high chemical selectivity, via electron binding energy chemical shifts. With a synchrotron light source, both core and valence electrons can be accessed, by tuning photon energies to relevant orbitals. Chemical selectivity of the method even includes indentifying different bonding types, such as van der Waals and hydrogen bonds, ionic bonding, and charge state. This allows us to study e.g. solvent effects of water on cluster structure and quantify the role of water on bonding type. Varying the photon energy also enables depth resolved profiling of the cluster composition, for example, to investigate if individual clusters are homogeneously mixed, or one or more components are surface partitioned. Using highly surface sensitive soft X-ray core PES (XPS) in particular, we can probe component fractionation, bonding structure, and charge state specifically in the topmost molecular surface layer of the clusters. In recent work, we have studied ion surface segregation in aqueous salt clusters, in terms of variations of anion/cation ratios with salt concentration, depth from the surface, and cluster size (Hautala et al., in preparation). Solvation of alkali halides and in particular ion bonding and segregation effects have previously been studied in bulk aqueous salt solutions, where PES revealed an enhancement of anion concentration in the surface layer (Cheng et al., 2012). Prior to these studies, evidence of ion enhanced chemical reactions with gases at the solution interface had also been found. Such phenomena related to aqueous ion solvation, interfacial effects, and ion pairing are highly relevant for both atmospheric and biological sciences (Jungwirth and Winter, 2008).

In our present experiments, water clusters with a mean size of about 100 molecules were generated using the EXMEC source and a variable number of RbBr monomers were doped into the clusters to vary the aqueous salt concentration. Photoelectron spectra were measured from both Rb cations, Br
anions, and water molecules in the clusters at each concentration, and the ratio of signals originating from solvated Rb cations and Br anions, respectively, was calculated. Preliminary results are shown in Figure 1, with the Br anion/Rb cation ratio as a function of aqueous RbBr concentration in the clusters (at this point in arbitrary units). For each concentration, two different photon energies were used to access different probing depths into the clusters. The more surface sensitive measurements (196 eV) show enhanced Br anion over Rb cation concentrations for the lowest salt concentrations, but as the aqueous concentration increases, the ion ratio tends towards unity. At the highest concentrations, clusters are almost pure salt and anions and cations are expected to appear in equal ratios at any depth. This is supported by more bulk sensitive measurements (250 eV), showing on average less enhancement of the anion at any concentration. These and our previously published results reveal changes in electronic structure with overall cluster size and surface/bulk characteristic of the system, which could profoundly impact the further fate of these clusters, e.g. in the chemically reactive atmosphere.

![Figure 1: Ion concentration ratios for RbBr–water nanoclusters as a function of aqueous salt concentration (oven temperature). Preliminary results.](image)

**CONCLUSIONS**

Recently, photoionization of atmospherically relevant aerosols produced in flow tube reactors (Kroll, et al., 2015) and smog chambers (Baeza-Romero, et al., 2016) has been studied, using synchrotron radiation in the vacuum ultraviolet (VUV) and extreme ultraviolet (EUV) range. Compared to core ionisation achieved with soft X-rays, valence photoionisation is not as element specific. In the soft X-ray regime, photoionization studies have been performed for clusters produced with electrospray ionisation. These clusters are inherently charged and were collected to an ion trap before exposing them to synchrotron radiation (Ryding, et al., 2014). To our knowledge, no electron spectroscopy studies in the soft X-ray regime have so far been carried out. Atomizers and nebulisers offer effective ways to produce aerosols from a stock solution or suspension. Coupled with an aerodynamic lens, which focuses aerosol particles into a beam, sufficient density of sub-micron particles can be achieved to directly probe their electronic structure using PES (Antonsson, et al., 2015). However, the method consume much larger amounts of sample than our cluster setup. Furthermore, the practical lower particle size limit is some tens of nanometers in diameter, whereas the cluster beam has no lower size limit.

The MUSCLE setup complements existing instrumentation, by offering sufficiently high sample densities to be coupled with an electron spectrometer, addressing a much lower size range than aerodynamic focusing allows, and producing neutral clusters, which may subsequently be charged...
in a controlled way. With its doping stage and collision cell the versatility of the MUSCLE setup
compares to the functionalities of conventional atmospheric reactor cells. In future work, more
evaporation sections could be added, just as a collision cell could be added for either direct use
or to provide a third pick-up region. This would also allow studying gas conditioning and chem-
cal reactions with the clusters produced. In principle, it is also possible to use the synchrotron
light for such cluster conditioning interactions, provided other means for subsequent characteriza-
tion, such as mass spectrometer, are available. Future efforts will also focus on further improving
photoelectron collection efficiency with a magnetic bottle spectrometer.

A common paradigm is that all clusters with similar compositions are similar in properties. Our
results for size-resolved aqueous salt clusters clearly show that this is not the case. Recent molecu-
lar dynamic simulations of homogeneous nucleation (Angéil et al., 2014) suggest that the structure
of equilibrium and non-equilibrium clusters may be different, but this has not been verified ex-
perimentally. The cluster source gives us a unique possibility to access states in the formation
process of new particles which are not accessible in the atmosphere in a controlled manner, as
well as to determine properties that allow us to evaluate their stability. In principle, it all comes
down to inter- and intramolecular forces. Knowledge of the detailed bonding structure in clusters
of different size, could, for example, help to constrain elusive concepts such surface tension and
other quasi-macroscopic cluster properties assumed in application of various nucleation theories,
inevitable for mesoscopic modelling of vapour–liquid nucleation. Such information would further
enable constraints on formation and growth rates of new atmospheric particles, especially under
circumstances such as harsh conditions or pristine, pre-industrial atmosphere, where direct obser-
vations are not possible. This work is part of the larger context of our recently granted ERC project
SURFACE, aiming to constrain the role of surface properties in atmospheric processes at a wide
range of different spatial and temporal scales.

ACKNOWLEDGEMENTS

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REFERENCES

PHASE CHANGES IN CARBOXYLIC ACID/WATER AEROSOLS: A MOLECULAR DYNAMICS STUDY

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Keywords: organic aerosol, adsorption, water, molecular simulations.

INTRODUCTION

Organic material is ubiquitous in the Earth’s atmosphere, coming from both natural sources and anthropogenic activities. The interactions between water and organic molecules are thus currently investigated in the context of atmospheric chemistry because liquid droplets and ice particles may scavenge some of these organic molecules from the atmosphere, thus modifying the atmospheric composition and chemistry. Organic matter represents an important fraction of the fine aerosol mass which comes also from sea salt, mineral dust, black carbon, sulfates, and nitrate ammonium whose relative abundance depends on, e.g., location, time, and meteorological conditions. Atmospheric aerosols play a central role on current atmospheric research, because aerosol particles have a direct effect on climate not only by scattering and absorbing solar radiation but also by scattering, absorbing, and emitting thermal radiation.

For all these reasons, a better understanding of the interactions between water and aerosols is urgent, in order to describe in detail the capacity of aerosols to serve as condensation nuclei for water, either in a liquid or a solid state. Given the complexity of aerosol chemistry, the modeling of systems by numerical simulations is an interesting way to describe the interactions between water molecules and aerosols at the molecular level.

METHODS

Molecular dynamics simulations were performed using the GROMACS program package (Abraham M.J., 2014) the interaction between a variable amount of water (modeling different humidity levels) and organic aerosols. Organic aerosols were modeled by small aggregates composed by carboxylic acids, i.e. formic, acetic, propionic and butyric acids (Vardanega, 2014; Radola, 2015).

The potential energy was calculated as the sum of dispersion-repulsion and Coulomb pairwise interactions. The dispersion-repulsion term was expressed with the standard Lennard-Jones (6-12) form. Short range interactions were neglected for atom pairs located at distances larger than the cut-off distance equal to 1.4 nm. The long-range part of the electrostatic contribution was evaluated with the Particle Mesh Ewald (PME) method. Calculations have been carried out in the temperature range of 150-275 K.

CONCLUSIONS

The results have evidenced two situations for the acid-water aggregates, corresponding either to water adsorption on large acid grains at very low temperatures or to the formation of demixed droplets consisting
of acid molecules adsorbed at the surface of water aggregates at higher temperatures and high water content. At low water content and high temperature, only a partial mixing between water and acid molecules is observed, in particular, at the surface of the aggregate. At moderate temperatures, an intermediate situation is obtained, which is characterized by a partial deliquescence of the acid aggregate.

Figure 1: Equilibrium geometry of butyric acid aggregates at 150 K (left) and 250 K (right) for 6:1 water:acid ratio. For the acid molecules, O, C and H atoms are represented by red, light blue, and white balls whereas all the atoms of water molecules are represented in dark blue for clarity.

The present results cannot be directly compared to any field measurements. However, they represent an additional step towards modeling of organic cloud condensation nuclei, leading to a deeper understanding of the complicated and environmentally relevant problem of heterogeneous nucleation of water. In particular, this study point out the complex effect of both temperature and humidity on the behavior of organic aerosols. They emphasize the need for further experimental and simulation works in this field.

ACKNOWLEDGEMENTS

Computations have been performed on the supercomputer facilities of the Mésocentre de calcul de Franche-Comté.

REFERENCES


PERFORMANCE EVALUATION OF A VTDMA-APM SYSTEM FOR THE VOLATILITY AND EFFECTIVE DENSITY OF ULTRAFINE PARTICLES

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Keywords: VOLATILITY, EFFECTIVE DENSITY, TANDEM DIFFERENTIAL MOBILITY ANALYZER, AEROSOL PARTICLE MASS ANALYZER.

INTRODUCTION

Ultrafine particles (UFPs, <100 nm) are ubiquitous in the ambient air and have significant impacts in climate, environmental and human health. The two major sources of UFPs are primary traffic emissions and secondary new particle formation, between which the former is more omnipresent in urban air during daytime hours and the latter can cover a spatial scale of 10-100s km (Kulmala et al., 2004). UFPs comprises predominantly of organic carbon (OC), followed by trace metal oxides, elemental carbon (EC), sulfate, nitrate and ammonium. Notably, the OC, NO$_3$ and NH$_4$+ are (semi)volatile materials that partition between particulate and gas phase under atmospheric conditions, whereas EC is a nonvolatile material below 300°C. Villani et al. (2008) showed that the loss of volatile material from UFPs could significantly increase or decrease their hygroscopicity. More recently, Schnitzler et al. (2014) and Graves et al. (2015) showed that soot aggregates undergo morphological restructuring after secondary organic aerosol coating process, thereby changing their effective density ($\rho_{\text{eff}}$). Conventional filter-based sampling and analytical methods lack the time-resolution to capture the dynamic nature of ambient UFPs. Aerosol mass spectrometer, on the other hand, is capable to measure the chemical composition of UFPs in real time, though it is costly and requires highly technical support. In between these two ends, tandem differential mobility analyzer (TDMA) occurs as a reasonable alternative that can provide indirect information on the mixing state (internal vs. external mixture) and chemical composition (i.e., volatile material) of particles in situ and in real time (Sakurai et al., 2005). When coupled with an Aerosol Particle Mass (APM) analyzer, the particle effective density can be examined for morphological characteristics (Hakala et al., 2017). The present study aims to develop and validate of a custom-made Volatility-TDMA system, coupled with an Aerosol Particle Mass (APM) analyzer for measuring the volatility and effective density of ambient ultrafine particles. The development focuses on the temperature uniformity and extended residence time in the thermodenuder, whereas the validation relies on laboratory-generated particles made of pure inorganics and organics, as well as internally-mixed organic-coated inorganics.

METHODS

We have constructed a thermodenuder comprising two aluminum blocks of 4-cm×4-cm×40-cm (W×H×L) with each has a straight-through cylindrical channel of 2.7 cm i.d. These two aluminum blocks were used as heating (volatilization) unit at 125°C and 300°C. Another cylindrical stainless steel tube of identical i.d. was used for room temperature conditioning of aerosol samples. Figure 1 gives the temperature profiles of at the centerline of the heating and cooling units at 125°C and 300°C. Also shown is the residence time (t$_r$) of the aerosol sample in the effective heating zone. This figure shows that the presented thermodenuder can provide a very stable and lengthy heating zone for the thermo-conditioning of aerosol samples. The resulting t$_r$ at 125°C and 300°C are 36.5 s and 23.9 s, respectively. Compared to thermodenuders from other studies, the presented thermodenuder has substantially longer t$_r$ to ensure that the equilibrium
between the vapor and aerosol phase has been reached. The volume-based removal efficiency of (NH$_4$)$_2$SO$_4$, H$_2$SO$_4$ and C$_8$H$_{16}$ monodisperse particles between 30-70 nm under varying thermo-conditioning temperature was determined. The results show that the three pure substances began to evaporate under low temperature at ~30°C. The near complete volatilization (>95% by volume) occurred at 140°C and 130°C for (NH$_4$)$_2$SO$_4$ and H$_2$SO$_4$, respectively. In comparison to earlier studies, the volatilization temperature ($T_{vol}$) for (NH$_4$)$_2$SO$_4$ in our study was substantially lower, indicating that vapor/particle equilibrium was not achieved in earlier studies due to the insufficient $t$. For the $T_{vol}$ of C$_8$H$_{16}$ was considerably lower at 60°C, highlighting the fact that organic compounds have substantially higher volatility than selected inorganic compounds. Internally-mixed particles composed of NaCl and DEHS were also used to validate the volatilization performance of the thermodenuder. The two chemical compounds have distinct $T_{vol}$ (>300°C vs. 60°C) and $\rho_{\text{tot}}$ (2165 kg m$^{-3}$ vs 912 kg m$^{-3}$). Figure 2 shows the selected size of the dry NaCl particles was 42.7 nm, which grew to size of 112.3 nm after coated with DEHS, and then returned to their original size of 42.7 nm after heating > 60°C. To verify that the coating of DEHS on NaCl and the volatilization of DEHS off the NaCl were successful, we attached the APM to the exit of the thermodenuder for mass and size measurements. The results show that the measured $\rho_{\text{eff}}$ of DEHS-coated NaCl of 112.3 nm was slightly lower (14%) than that of the $\rho_{\text{tot}}$. Above 60°C the DEHS was completely removed from the NaCl and thus the measured $\rho_{\text{eff}}$ was only slightly lower (<18%) than the material density of dry NaCl. The measured dynamic shape factor ($\chi$) were also in line with expected $\chi$ of 1.08 for dry NaCl. These results indicate that the presented denuder has good volatilization performance in measuring the volatility of UFPs and that the coupled APM can simultaneously measure the particle mass for the determination of $\rho_{\text{eff}}$ as well as the morphological characteristics of UFPs.

![Graph showing temperature profile in the thermodenuder at 125°C and 300°C.](image_url)

Figure 1. The temperature profile in the thermodenuder at 125°C and 300°C.
Figure 2. The changes in particle size of NaCl before/after DEHS coating and after heating to 60°C.

CONCLUSIONS

A custom-made VTDMA-APM system has been developed and validated for measuring the volatility and effective density of ambient ultrafine particles. The results show that the temperature profile is very stable throughout the entire length of the thermodenuder and the resulted residence times are substantially longer than those presented in earlier studies. Using pure (NH₄)₂SO₄, H₂SO₄ and C₆H₆ monodisperse particles, the results show that volatilization temperatures measured by the present VTDMA are generally lower than those from earlier studies, indicating that the vapor/particle equilibrium may not be achieved in those studies. Using internally-mixed particles composed of NaCl coated with DEHS, the VTDMA-APM system is capable to measure the volatility and effective density with reasonable accuracy.

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REFERENCES


TEMPERATURE DEPENDENT SPECTROSCOPY OF SINGLE MODEL SEA SPRAY AEROSOL

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Keywords: Single particle, sea spray aerosol, hygroscopicity, spectroscopy.

INTRODUCTION

Recent field and laboratory experiments suggest that aerosol generated from the ocean, also called sea spray aerosol (SSA), may act as cloud condensation nuclei (Wang et al. 2015) as well as ice nuclei (DeMott et al. 2016); (Worringen et al. 2015). Additionally, size-resolved measurements on nascent SSA generated in an enclosed, wave-breaking channel provided identification and quantification of a number of chemical species, which include a significant fraction of aliphatic fatty acids and dicarboxylic acids (Cochran et al. 2016). SSA contain a complex array of inorganic and organic molecules, but it is useful study simplified chemical systems in the laboratory that represent relevant classes of molecules to benchmark their contributions to the hygroscopicity and ice nucleating ability of SSA. Previous low-temperature single particle experiments have included substrate-deposited techniques (Schill et al. 2014), optical trapping (Ruberto et al. 2016) and electrodynamic balance with Mie scattering (Tong et al. 2015). Herein we describe a new instrument for measuring the temperature-dependent properties of mixed inorganic-organic SSA model systems that uses electrodynamic trapping in concert with Mie and Raman scattering. Single microdroplets are confined at atmospheric pressure under controlled relative humidity and temperature as low as -40 °C for spectroscopic analyses of growth, evaporation, nucleation, and heterogeneous chemistry over extended time scales (hours). Initial characterization experiments using aqueous ammonium nitrate demonstrate the versatile capabilities of the apparatus, and set the stage for further chemical systems to be explored.

METHODS

These experiments combine light scattering and optical spectroscopies with single particle trapping techniques using an atmospheric-pressure quadrupole ion trap, a type of electrodynamic balance (EDB). The experimental approach involves generating charged aerosol microdroplets with known chemical composition and fixed diameter using a piezoelectric droplet generator and levitating in an atmospheric pressure quadrupole ion trap under controlled conditions of temperature and relative humidity for subsequent light scattering analysis. A sophisticated interface has been developed for computer-controlling the temperature, relative humidity and ambient pressure, synchronization and automation of droplet generation, and recording the optical spectra of charged SSA. Figure 1 shows a schematic of the EDB apparatus, which is equipped with computer-regulated mass flow controllers for control of water vapor partial pressure, as well as a free-piston, low-vibration cold head for achieving low temperatures in the trapping volume. Initial experiments have been carried out for characterizing particle size, charge, and morphology.
The EDB was constructed using the open design of Gerlich and co-workers (Schlemmer, Schlemmer et al. 1999); (Schlemmer et al. 2001); (Trevitt et al. 2007) for multidirectional optical access. The basic trap design includes two end-caps to which AC voltage is applied and, instead of a hyperbolic central ring electrode, eight rods are arranged to which DC voltage is applied. This geometry produces an approximate quadrupolar field for trapping single particles and the open geometry provides multiple optical access pathways and a wide collection angle for photons scattered from a trapped particle, as shown in Figure 2. A high repetition rate kHz Nd:YAG 532 nm laser (RPMC Wedge XF) with < 700 ps pulse width and remote controlled power output is aligned axially through the conical endcap electrodes. The laser is focused in the trap center and serves as the excitation source for both Mie and Raman scattering. Particle size and phase are determined from the Mie scattering phase functions, collected orthogonally using a high-speed CMOS camera. Particle diameter is calculated using the geometric optics approximation, which provides good agreement with Mie theory calculations for diameters larger than 1.7 micron (Glentschnig et al. 1981). A size calibration curve in Fig 3 generated from scattering phase functions of three diameters of calibration spheres is used for in-situ particle sizing.
Additionally, chemical analysis is achieved using Raman spectroscopy. Raman spectroscopy has previously been used to quantify oxidation of organic compounds (Dennis-Smith et al. 2014), and identify the hydration state (Ishizaka et al. 2014) and chemical composition (Chan et al. 2006) of single aerosols. Scattered light is collected at 90° using an f/2 lens, and focused into a high O-H fiber optic cable which is mounted on a Czerny-Turner 0.275 m monochromator (Acton SpectraPro 275). The spectrometer is equipped with a 600 g mm⁻¹ grating and a high-speed CCD (Horiba Synchrony) detector for recording multiplexed spectra at a high rate. This same optical configuration has also been used for measurement of fluorescence spectra. Initial experimental efforts have focused on calibration of the apparatus using well-studied chemical systems such as aqueous sodium chloride, ammonium nitrate, and malonic acid. Figure 4 shows a spectrum of a single 78 μm aqueous ammonium nitrate (AN) microdroplet which was trapped under humidified conditions, and compared with a representative 5M bulk solution of AN contained in a micro-cuvette centered in the EDB.

Figure 4. Raman spectra of bulk ammonium nitrate in a glass cuvette (black dashed) and of a single trapped ammonium nitrate droplet (blue solid). Spectra were both collected in the configuration described in Fig. 2 and have been normalized to the NO₃ peak.

Following initial characterization experiments of the new apparatus, efforts have focused on low-temperature capabilities. Data of temperature-dependent and specifically low-temperature measurements of ammonium nitrate, sodium chloride, and mixtures with atmospherically relevant organics such as aliphatic acids and monosaccharides will be presented.
CONCLUSIONS

In this abstract a new variable-temperature EDB system dedicated to studying phase change behavior of model SSA has been discussed. The development and application of temperature-controlled single-particle analytical techniques will provide transformative insights in aerosol impact on climate and the environment. Measurements on trapped particles remove uncertainties associated with particle-substrate interactions and may reveal phenomena that are lost in ensemble averages inherent in bulk measurements.

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REFERENCES


COMPUTATIONAL STUDY OF THE CHEMICAL IONIZATION OF HIGHLY OXIDIZED OH-INITIATED OXIDATION PRODUCTS OF BUTADIENE USING DIFFERENT REAGENT IONS

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Keywords: CHEMICAL IONIZATION, HOMs, OH OXIDATION.

INTRODUCTION

Chemical ionization is commonly used for the detection of neutral molecules in the gas phase. Different reagent ions, such as nitrate (NO₃⁻) and iodide (I⁻), have recently been used to detect various autoxidation products of volatile organic compounds (VOCs) in the ambient air and in laboratory experiments. There are also other reagent ions such as trifluoromethanolate (CF₃O⁻) and acetate (CH₃C(O)O⁻) that have previously been used to detect small acids.

In addition to adduct formation, some of the reagent ions also react with the sample molecules. For instance CH₃C(O)O⁻ can deprotonate many carboxylic and peroxy acids, and peroxy acids have been detected as dehydroxylation products using I⁻ as the reagent ion. Using CF₃O⁻, some sample molecules can abstract a fluoride ion from the reagent ion, leaving a neutral CF₂O. This fluoride exchange reaction has been observed with for instance HNO₃ and HCl.

We have studied the different ionization mechanisms of these four reagent ions. In addition, the potential of trifluoroacetate (CF₃C(O)O⁻) as a reagent ion was computationally tested. As sample molecules we have used several products from the OH-initiated oxidation of butadiene. While small enough to be computationally inexpensive, the studied molecules resemble highly oxidized atmospherically relevant autoxidation products, and contain both hydroxyl and hydroperoxy groups. To investigate the effect of water on the chemical ionization process, we also consider a situation where the sample molecule is ionized by a reagent ion hydrate (for instance (H₂O)ₙ·I⁻, where n = 1, 2, 3).

METHODS

We calculated the formation free energies and enthalpies of the reagent ion – sample molecule -clusters, at DLPNO-CCSD(T)/def2-QZVPP//MP2-B97xD/aug-cc-pVTZ level of theory (aug-cc-pVTZ-PP basis set for I⁻).
CONCLUSIONS

The binding (in terms of the standard Gibbs free energy, at the \textit{ab} initio level of theory) between the reagent ions and the sample molecules is strongest for CH$_3$C(O)O$^-$ and weakest for I$^-$. The binding of NO$_3^-$, CF$_3$O$^-$ and CF$_3$C(O)O$^-$ is slightly stronger than that of I$^-$, NO$_3^-$ having the weakest binding of the three with most of the studied sample molecules, depending on the functional groups of the sample molecule. For instance, carbonyl groups in the sample molecule make the binding with NO$_3^-$ stronger relative CF$_3$C(O)O$^-$. Due to the strong binding of the HNO$_3$(NO$_3^-$) dimer, the detection efficiencies of most of the butadiene oxidation products studied here with nitrate CIMS should be very low. The binding with CF$_3$O$^-$ and CF$_3$C(O)O$^-$ is similarly weak, but without the competing dimer formation, the detection efficiency should be higher.

Figure 1 shows the formation free energies of all of the reagent ions clustering with one of the sample molecules, (Z)-4-hydroperoxybut-2-en-1-ol. For this sample molecule, our calculations show that chemical ionization through a fluoride exchange with CF$_3$O$^-$ is also energetically favorable, whereas deprotonation by CH$_3$C(O)O$^-$ is unfavorable.

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INVESTIGATING THE GAS-PHASE FORMATION OF ORGANIC SULFUR COMPOUNDS FROM ATMOSPHERIC VOLATILE ORGANIC COMPOUND OXIDATION REACTIONS

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Keywords: Aerosol precursors, Organosulfur compounds, Atmospheric oxidation, Autoxidation.

INTRODUCTION

Atmospheric nanoparticles affect our health and environment. Currently they are estimated to cause millions of premature deaths per year and significantly reduce the standard of living in many areas of the globe. On climate aerosols exert an influence by absorbing and reflecting solar radiation as well as by acting as seed for new cloud droplets. Around 20-90% of submicron aerosol mass constitutes of secondary organic aerosol (SOA) that has been derived from gas-phase transformation of volatile organic compounds (VOC) (Jimenez et al. 2009). Despite its immense importance for trace gas removal and radiation balance of the atmosphere the details of the SOA formation at a molecular level have remained elusive.

By recent investigations it has become evident that very low volatile compounds, such as sulfuric acid, are needed in order to form the smallest of the particles, on top of which the higher volatile compounds can then cluster. It has also become obvious that sulfuric acid alone is not enough to account for the atmospheric particle formation rates, and that organics are needed to tie the gap (Donahue et al. 2013). Very recently so-called highly oxidized multifunctional compounds (=HOMs) were discovered and connected to the early steps of SOA formation and growth (Ehn et al. 2014). They are formed by autoxidation sequences (Crounse et al. 2013, Rissanen et al. 2014) creating a multitude of chemical functionalities, the most abundant presumably being carboxyls and hydroperoxides. However, since then it has been suggested that only a subset of these species will actually have low enough vapor pressures to act as aerosol embryos (Kurtén et al. 2016). Thus in order to sustain the observed ambient particle formation rates (as well as early-growth rates), species with extremely low vapor pressures are required.

Organic sulfur species such as organosulfates and organosulfonates could have the very low vapor pressures needed to kick-start SOA formation in the gas-phase. These species have been previously inferred from ambient field measurements using offline aerosol analysis methods (e.g. Nguyen et al. 2014). The most commonly applied online method of investigating nanoparticle composition is aerosol mass spectrometer (AMS). However, it does not generally differentiate between organic and inorganic sulfates. From a previous AMS study it was reported that organosulfates could have accounted for about 12% of the AMS detected sulfates (Farmer et al. 2010). A more recent study (Brüggemann et al. 2017) reported as high as 47% of the compounds from filter samples to contain sulfur.

METHODS

The formation of organosulfur compounds in O3 initiated oxidation of terpenoids isoprene (C10H16) and β-caryophyllene (C15H24), and a common monoterpene surrogate cyclohexene (C6H10), were investigated in tubular flow reactors. Quartz flow tubes with special needle injectors were applied to enable
photochemical perturbation of the reacting gas mixture down to UV wavelengths, and addition of reagents in different times during the evolution of the reacting gas mixture. The organic sulfur compounds were detected directly from the on-axis sampled gas stream using either iodide (I⁻), nitrate (NO₃⁻) or proton transfer (H⁺) as the reagent ion scheme in a chemical ionization atmospheric pressure interface time-of-flight mass spectrometer (CI-API-ToF; Junninen et al. 2010, Kurtén et al. 2011, Jordan et al. 2009). The identity of the product clusters was further scrutinized by a nitrate chemical ionization quadrupole mass spectrometer in experiments where gradually increased defragmentation field strength could be used to infer more about the chemical identities of the clusters/molecules detected. In addition to laboratory experiments, quantum chemical computations were employed to investigate the formation pathways and to infer potential product structures by comparison to experimentally determined cluster binding energies.

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REFERENCES

MEASURING THE TEMPERATURE RESPONSE OF HIGHLY OXIDIZED MULTIFUNCTIONAL (HOM) MOLECULES IN ALPHA-PINENE OXIDATION IN A COLD-ROOM SMOG CHAMBER.

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Keywords: HOMs, CI-API-TOF, Cold-Room SMOG Chamber, Temperature.

INTRODUCTION

The formation of Highly Oxidized Multifunctional (HOM) molecules in the atmosphere was shown to result from the oxidation of biogenic vapors released by terrestrial vegetation (Ehn et al., 2012). HOM were recently suggested to be key contributors to Secondary Organic Aerosol (SOA) formation (Ehn et al., 2014) and nano-particle growth (Tröstl et al., 2016), which influences cloud processes and thereby climate. In this work, we present our latest results of HOM measurements done at the Aarhus University cold-room smog chamber (Kristensen et al., 2017) which can simulate atmospheric processes at temperatures ranging from 20 °C down to -16 °C. With this study, we aimed at better characterizing the chemical processes involved in the formation and the evolution of HOMs when they are produced upon α-pinene oxidation at different temperatures.

METHODS

A high-resolution nitrate-based Chemical Ionization Atmospheric Pressure interface Time-Of-Flight (CI-API-TOF) mass spectrometer (API-TOF, Tofwerk AG, Thun, Switzerland and Aerodyne Research Inc., USA), described in Jokinen et al. (2012), was deployed to measure the gas phase highly oxidized compounds produced upon α-pinene ozonolysis in a 5 m³ environmental chamber. The experiments were operated in a batch sampling mode with initially 100 ppb of ozone dispersed in filtered air, exempt of particles. Alpha-pinene concentrations of 10 and 50 ppb were used, and experiments were performed at 20, 0 and -15 °C. (cf. separate abstract by Kristensen et al. 2017).

With a high number of oxygen atoms, α-pinene derived HOMs are usually seen in the mass range 300-600 Th and present a typical chemical composition of C_{10}H_{14-16}O_{7-11} (monomers) and C_{19-26}H_{28-32}O_{10-18} (dimers). Figure 1 shows HOM-monomer mass spectra, in the range 300-400 Th, at 20 °C, 0 °C and -15 °C, averaged over 10 minutes sampling after the injection of α-pinene at high concentration. From this example, a significant decrease of signal, and thus in concentration, can be seen the cooler the reaction temperature is. Additionally, a change in the distribution of the most abundant species can be depicted between the different temperatures at which the spectra were recorded.
Figure 1. Mass spectra of high-mass compounds present in the gas phase during high VOC load experiments, at 20 °C (red), 0 °C (orange) and -15 °C (blue). Most abundant species, in C₁₀ typical carbon skeleton, were tagged and identified from first analysis of high resolution data. The presented data were acquired from a few minutes following the VOC injection and averaged over 10 minutes.

Further analysis were done, focused of the evolution of specifically targeted species of know chemical composition, from which we aim at characterizing the behavior of the molecules starting from the injection of the precursor to several hours after the start of the experiments. Figure 2 is an example of the time traces recorded during the high load experiments at the aforementioned temperatures. Herein, it is possible to depict the main steps of an experiment (i.e. background, injection and stabilization of the HOM compound produced) and furthermore characterize the formation rate for the selected chemical entities.

Figure 2. High resolution time traces for selected compounds formed in high α-pinenone concentrations. The chosen species have a chemical formula in C₁₀H₁₄ panel a) and C₁₀H₁₆ panel b) containing 7, 9 or 11 oxygen atoms and are measured as cluster with nitrates, as reagent ions. These preliminary time series are presented for 20 °C (red), 0 °C (orange) and -15 °C (blue).
CONCLUSIONS

With this ongoing work, we investigate the variability of the HOMs signal at different temperatures by comparing the differences in both the chemical composition and the abundance. Colder temperatures clearly slowed down the rate of HOMs production. Similarly, the temporal evolution of several compounds were seen to change as a function of temperature, suggesting changes in volatility from semi-volatile to low-volatile. Further analysis will focus on obtaining a more detailed understanding of chemical formation pathways and physico-chemical properties of these highly oxidized molecules, especially linking them to the formation of SOA.

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REFERENCES


HOM concentrations and their contributions to initial growth at the boreal forest of Finland (SMEAR II station) and urban China (SORPES station)

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Key words: MALTE-BOX model, HOM formation, Nucleation, Initial growth

INTRODUCTION

Highly oxidized multifunctional organic compounds (HOM) play key roles in new particle formation (NPF) and thereby influence the climate and air quality. HOM formation and NPF mechanism is well studied at SMEAR II station, a boreal forest site. However, as one of the most economically invigorating and densely populated countries, China, the measurements of HOM are rare. The measurements at SORPES station, a station in urban clusters of Yangtze River Delta region, show more frequent NPF events and stronger formation and growth rates than SMEAR II station [Qi et al., 2015]. This study uses the MALTE-BOX model to simulate the HOM and NPF at SMEAR II and SORPES. By comparing the modeling results at two sites, the differences of HOM concentration and their contributions to initial growth are investigated.

METHODS

This study used the MALTE-BOX model (the model to predict new aerosol formation in the lower troposphere), a zero-dimensional model, which includes several modules for the simulation of chemical and aerosol dynamical processes [Boy et al., 2006].

The gas-phase chemistry was simulated using the Master Chemical Mechanism version 3.3 (MCMv3.3, http://mcm.leeds.ac.uk/MCM/). It is a near-explicit oxidation scheme. A new HOM formation module, which is constructed based on the oxidation of monoterpene [Ehn et al., 2014], was added into the MCMv3.3. The aerosol dynamical processes were simulated with the size-segregated aerosol model, UHMA (University of Helsinki Multicomponent Aerosol model). A full-moving sectional approach with 60 bins from 1 nm to 20 µm in diameter was used. The particle number size distributions were then mapped onto a fixed diameter grid in order to get a dN/dlogDp distribution. For the smallest size bin, the formation rates of newly formed particles were estimated by the kinetic nucleation theory of sulfuric acid, i.e. $J=k*[H_2SO_4]^2$. The kinetic coefficient $k$ was set for each day to achieve the highest correlation compared to the measured newly formed particles. Based on the calculated
saturation vapor pressures, 653 species including ELVOCs (HOM who have extremely saturation vapor pressures are defined as ELVOCs), SVOCs (HOM and other gas vapors who have semi-low saturation vapor pressures are defined as SVOCs) and sulfuric acid were chosen as condensing vapors in the condensation module of UHMA. H$_2$SO$_4$ was considered as a non-volatile condensing vapor. The coagulation and dry deposition processes were included in the model as well. The parameterization of boundary layer dilution was added in MALTE-BOX so that the simulated particle volume concentrations at daytime are similar with measurement.

The measurement variables, i.e. meteorological conditions (Temperature, Relatively Humidity, Pressure, Radiation), trace gases concentrations (SO$_2$, O$_3$, NO, NO$_2$, CO) and VOCs (ethylene, ethane, propane, acetone, methyl vinyl ketone, n-Butane, benzene, isoprene and monoterpenes), were input into the MALTE-BOX model every 10 min. As monoterpenes were not measured by GC-MS at SORPES, monoterpane concentrations at SORPES were simulated by WRF-CHEM. Using WRF-CHEM data in MALTE-BOX was proved to work well in NPF simulation [Huang et al., 2016]. The measured aerosol number size distribution was read into the model during the first five hours. For steadying the model, the chemistry scheme was running for 24 hours before the aerosol module was switched on.

RESULTS AND CONCLUSIONS

A HOM formation module is added into the MCM so that the comprehensive HOM concentration can be simulated. The simulations were done for the cases (five cases) at SMEAR II firstly so that the performance of model can be evaluated. For HOM monomers and dimers, the model works well at daytime while tending to underestimate the HOM monomers and overestimate the HOM dimer at nighttime (Fig 1a, b). The simulated HOM nitrate concentrations are comparable with the measurements but still overestimate to a certain extent at nighttime (Fig 1c). The simulated HOM peroxy radicals concentrations are similar with measurement at daytime but lower than measurements at nighttime. In general, considering the uncertainties of the CI-API-TOF in measuring HOM, the model provides an acceptable agreement between simulated and measured HOM concentrations.

Although no measurements of HOM at SORPES exist at this time, the simulated HOM concentrations (solid black lines) at SORPES are plotted in Fig 1. HOM monomers concentrations are higher at SORPES than at SMEAR II especially at 14:00 LT when O$_3$ concentrations and radiation are high. High O$_3$ and radiation, causing high atmospheric oxidation capacity, together with high VOCs, like monoterpene and benzene, can produce sufficient HOM peroxy radicals (Fig 1d) and form high values of HOM monomers. However, the HOM dimers concentrations at SORPES are much lower than at SMEAR II. It is mainly because high NO concentrations at SORPES suppress the formation of the organic nitrates (HOM-nitrates). The HOM-nitrate concentrations at SORPES are two orders of magnitude higher than at SMEAR II (Fig 1c). The simulated HOM concentrations when the boundary layer dilution was not considered are also plotted in Fig 1a-c. The vertical convections of HOM have a huge effect on the simulations of HOM. Therefore, 1D model runs are required to get a better understanding of the vertical mixing (work in progress).
Figure 1 Average simulated and measured diurnal cycles of (a) HOM monomers, (b) HOM dimers, (c) HOM nitrates and (d) HOM peroxy radicals at SMEAR II and SORPES. Note: Measurement and simulation average and ±1 standard deviation (shaded area) at SMEAR II are in blue and red, respectively; simulation average at SORPES are in black solid lines; simulation average without boundary dilution taken into account at SORPES are in black dash lines. The small figure in Fig 1c is the simulated HOM nitrates concentration at SORPES.

The relative contributions of precursor vapors to the growth of particles at SMEAR II and SORPES are quite different (Fig 2). Through the high gas-phase sulfuric acid concentration at SORPES, the sulfuric acid can contribute up to almost 60% of the growth of sub-3 nm particles and can even contribute 10% of the growth of 10-100 nm particles at SORPES. At SMEAR II, the sulfuric acid only adds about 30% to the initial growth (the growth of sub-3 nm particle) of newly formed particle and less as 1 % for larger sizes. The HOM monomers contribute less to the growth at SORPES than at SMEAR II and also play a weak role in the initial growth at SORPES. The HOM carbonyls contribute strong to the growth at both sites. Because high values of HOM nitrate at SORPES, HOM nitrates contribute about 20% of the growth of 3-30 nm particles while adds only insignificant to the growth at SMEAR II. Therefore, nitrogen oxide, as one important pollutant in urban areas, can induce high formation of organic nitrate and then increase the particles budgets. The HOM nitrate mostly contribute to particles with sizes >3 nm because the higher saturation vapor pressures compared to the other HOM. HOM dimers are one important contributor in the initial growth at SMEAR II but only contribute about 2% of initial growth at SORPES. SVOCs contribute more to growth at SMEAR II than at SORPES. In general, this study concludes that sulfuric acid and HOM nitrate contribute strongly to the growth of newly formed particles in urban
sites like SORPES whereas HOM monomers and dimers have strong influence at the rural site SMEAR II.

Figure 2 The averaged relative contributions of precursor vapors to the growth of sub-100 nm particles on NPF event days at (a) SMEAR II and (b) SORPES.

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REFERENCES
Atmospheric aerosols are solid or liquid particles suspended in the air. Despite their small size, they have strong influence on our everyday lives. To begin with, aerosol particles decrease the air quality and visibility but they also have an effect on the Earth’s radiative forcing as they scatter the incoming solar radiation directly or via cloud formation as a net effect. Atmospheric aerosols can be directly emitted into the atmosphere as particles or they arise from gas-to-particle transitions. In the latter case, they are called secondary aerosols.

A significant fraction of tropospheric aerosols consists of secondary organic aerosol (SOA). It originates from the oxidation of volatile organic compounds (VOCs), such as isoprene or monoterpenes. Recent studies have highlighted the formation of highly oxidized multifunctional compounds (HOMs) in both gas (Ehn et al., 2014) and particle phases (Lopez-Hilfiker et al., 2016). HOMs are formed from the autoxidation of peroxy (RO₂) radicals and have a very low vapor pressure. As a result, they easily condense onto aerosol surfaces and contribute to SOA formation. Although the importance of HOMs in new particle formation has been recently demonstrated, the formation pathways as well as the fate of HOMs remain still unclear. Potential multiphase reactions, such as decomposition (Krapf et al., 2016) or reactive uptake might be important and could further affect the chemical composition as well as the mass of SOA. For example, isoprene-derived SOA has been demonstrated to mainly form through acid-catalyzed reactive uptake of isoprene oxidation products (Surratt et al., 2010) underlying that multiphase chemistry plays an important role in SOA formation.

Atmospheric nitrogen oxides (NOₓ), mainly anthropogenic in origin, react with RO₂ radicals formed from the oxidation of VOCs, generating semi-volatile organic nitrates (ON) that can also significantly contribute to the SOA. It was recently shown that the lifetime of ON in the particles is short, only a couple of hours, due to efficient hydrolysis in the particles (e.g. Lee et al., 2016). Despite that, the impacts of such processes in SOA formation and aging as well as the characterization of the products formed still remain incompletely understood. Here, we investigate the importance of aerosol acidity in the hydrolysis reactions of ONs and their fate in the presence of sulfate aerosol of varying acidity under different relative humidity (RH) conditions. The ONs were formed from the ozonolysis of α-pinene, a common monoterpene emitted from boreal forests, in the presence of NOₓ.

The experiments were conducted in a 2 m³ Teflon chamber using three different RH stages based on the literature: 1) at 50% RH, when atomized ammonium sulfate (AS) and ammonium bisulfate (ABS) seed particles have approximately equal aerosol liquid water content (ALW), 2) at 30% RH, when the AS particles effloresce yet ABS particles have moderate ALW, and 3) under non-humidified, “dry” conditions, where AS particles again effloresce, but ABS particles have only minor ALW. The chamber
was operated in a continuous flow mode having a residence time of 50 minutes. α-pinene, ozone, NO and seed aerosol particles (AS or ABS) were injected with constant flows.

The chemical composition of aerosol particles was characterized with an Aerodyne Long Time-of-Flight Aerosol Mass Spectrometer (L-ToF-AMS; DeCarlo et al., 2006) and a Filter Inlet for Gases and AEROsols (FIGAERO; Lopez-Hilfiker et al., 2014) mounted in front of a Long Time-of-Flight Iodide-Adduct Chemical-Ionization Mass Spectrometer (L-ToF-I-CIMS; Lee et al., 2014). Both of these mass spectrometers were carrying extended ToF-chambers allowing higher mass resolutions that facilitated better separation of nitrogen containing peaks from other organics.

Since the AMS uses flash vaporization at 600°C and hard ionization (electron impact, 70 eV), particulate organic nitrates, for instance, are mainly detected as NO+ fragments (Farmer et al., 2010). However, also other N-containing fragments are formed, such as CₓHᵧNᵦ⁺ (e.g. Rollins et al., 2010). The abundance of these fragments will be compared to ON standards. The FIGAERO-CIMS, on the other hand, collects the particles on a filter and heats the sample up to 200°C before softly ionizing it. This procedure provides more detailed information of the chemical composition.

In this work, the fate of ON under a wide range of ALW and acidities will be presented with extremely high resolution. The abundance of CₓHᵧNₒ₋ₓ and CₓHᵧNᵦ⁺ fragments under these conditions, as well as the behavior of the more common NO+ and NO₂⁺ ion fragments will be discussed. Moreover, a detailed analysis of the level of functionalization as well as the evolution of the identified nitrogen containing compounds under the different conditions will be presented.

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REFERENCES


Spatial and temporal variation of haze in China from 1961 to 2012

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Abstract: The purpose of this study is to analyze the climatic characteristics and long-term spatial and temporal variations of haze occurrence in China. The impact factors of haze trends are also discussed. Meteorological data from 1961 to 2012 and daily PM10 concentration from 2003 to 2012 are employed in this study. The results indicate that the annual-average hazy days of all stations have been increasing rapidly from 4 days in 1961 to 18 days in 2012. Maximum haze days occur in winter (41.1%) and minimum haze days occur in summer (10.4%). During 1961-2012, the high occurrence areas of haze have shifted from central to south and east of China. Beijing-Tianjin-Hebei (Jing-Jin-Ji) region, Shanxi, Shaanxi, and Henan Province are the high occurrence areas of haze. While, the Yangtze River Delta (YRD) and the Pearl River Delta (PRD) have become the regions with high haze occurrences in the last 25 years. Temperature and pressure are positively correlated with the number of haze days. However, wind, relative humidity, precipitation, and sunshine durations are negatively correlated with the number of haze days. The key meteorological factors' affecting the formation and dissipation of the haze vary with high and low altitudes, and is closely related to anthropogenic activities. In recent years, the anthropogenic activities have played more important role on haze occurrences compared with the meteorological factors.
Keywords: China; haze; spatial distribution; interannual trend; meteorological factors; anthropogenic activities

Fig. 7 - Spatial distribution of average haze days in China (28/2015/160).
WHAT HAPPENS TO SULFURIC ACID-AMINE CLUSTERS INSIDE THE API-TOF?

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Keywords: API-TOF, CLUSTER, SULFURIC ACID, AMINES.

INTRODUCTION

Chemical Ionization Atmospheric Pressure interface Time Of Flight mass spectrometer (CI-API-TOF) has revolutionized the study of atmospheric new particle formation. This instrument is able to detect small clusters which are involved in the first stages of new particle formation, even at environmental low concentration. It can give the elemental composition of clusters and an estimate of their concentration, if the instrument is carefully calibrated. Moreover, the development of highly selective chemical ionization techniques (e.g. using nitrate as reagent ion) can allow the selective ionization of interested clusters, eliminating the interferences from all other molecules and clusters present in the atmosphere (Jokinen et al., 2012). Although the use of the CI-API-TOF is exponentially grown in the last years, a systematic study on the fate of atmospheric clusters inside the instrument has not been carried out until now. It has been reported that clusters can undergo transformation inside the instrument, in particular the charging process, the low pressure and also energetic collisions with neutral molecules can affect the molecular composition of clusters (Kürten et al., 2014). This hypothesis is also supported by computational studies, indeed, it has been shown that theoretical models predict a higher cluster concentration than the measured concentration (Olenius et al., 2013). This discrepancy has been attributed to the cluster fragmentation process inside the instrument which is not taken into account.

Sulfuric acid is a key species in new particle formation, and together with ammonia and amines, it seems to be involved in many nucleation processes (Vehkamäki and Riipinen, 2012). In this study we investigated the fate of sulfuric acid and sulfuric acid-amine clusters inside the API-TOF to determine the factors and the conditions that lead to transformation of clusters inside the instrument. We adopted two techniques to reach our goals: we used a CI-API-TOF with nitrate as reagent ion and we combined a Differential Mobility Analyzer (DMA) with the API-TOF. These two techniques allow us to evaluate the effects of the chemical ionization (using the CI-API-TOF) on cluster composition and to distinguish the impact of voltages applied in the API section for each size ions distribution selected by the DMA.

METHODS

The experiments were carried out in the laboratory and sulfuric acid (H₂SO₄) clusters were produced by a gas saturator. The sulfuric acid-ammonia clusters were generated by mixing an airflow containing sulfuric acid vapors and an ammonia (NH₃) flow (from an NH₃ standard gas tank) in a small quartz tube. The experiments were carried out at different relative humidity (RH) and different sulfuric acid and ammonia concentrations. The clusters were then injected into the CI-API-TOF. The initial tuning of the instrument was a standard tuning to optimize sensibility and resolution. After observing a stable signal of sulfuric acid and sulfuric acid-ammonia clusters, the tuning was changed to evaluate the effect of applied electric field on the clusters signal.

A schematic representation of the CI-API-TOF is shown in Figure 1. Clusters enter in the chemical ionization (CI) chamber where nitrate ions and its cluster with nitric acid react with sulfuric acid (and its clusters) through the following proton transfer reaction:
The ions are then guided inside the atmospheric pressure interface (API) through a series of three vacuum chambers before arriving to the time-of-flight mass spectrometer. The pressure decreases between successive chambers until arriving to $10^{-6}$ mbar in the mass spectrometer. In the first two chambers (SSQ and BSQ) the ions are guided through quadrupoles (Quad1 and Quad2), while in the last chamber (PB) several lenses focus the ions. In total, 27 voltages and 2 radio frequencies are applied to APi-TOF, most of which can be changed to optimize the results as a function of the specific application of the instrument. In this work we evaluated the effects of the voltages applied to SSB and BSQ chambers without changing the radio frequencies.

In order to evaluate the effects of applied voltages on mono-disperse particles (clusters) we combined the APi-TOF with a High Resolution Differential Mobility Analyzer (HR-DMA). We connected the DMA in front of the APi-TOF, allowing us to inject into the APi-TOF mono-mobile size ions distribution. Successively we changed the tuning of the APi-TOF to assess its impact on fragmentation of the selected ions. We produced sulfuric acid and sulfuric acid-dimethylamine clusters in a standard laboratory setup using electrospray ionization.

CONCLUSIONS

In this study we demonstrate that the tuning of the instrument can significantly affect the sensibility of the instrument as well as the fragmentation and evaporation of clusters. The fragmentation seems to happen mainly in the first chamber (SSQ) where the pressure is relatively high (~2 mbar). Here, the charged clusters are accelerated by an electric field and can produce energetic collisions with neutral molecules. As expected, we observed a more significant fragmentation when high voltages are applied to Quad1 and Quad2, moreover the voltage difference between the SSQ and BSQ chamber seems to have an important impact on cluster fragmentation.

This preliminary study allows to better understand the fate of clusters inside the APi-TOF and it could be useful to correctly determinate the concentration and composition of sulfuric acid-amine clusters in the atmosphere. Moreover, it lays the bases for developing a theoretical model to describe and predict the fate of clusters inside the APi-TOF.

![Figure 1. Schematic representation of a section of the CI-API-TOF and possible fate of atmospheric clusters inside the instrument.](image-url)
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REFERENCES


INTRAMOLECULAR H-MIGRATIONS IN CERTAIN TYPES OF PEROXY RADICALS IN THE URBAN ATMOSPHERE

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Keywords: Peroxy radicals; Intramolecular H-migration; Atmospheric Oxidation Mechanism; Mass Spectrometry.

INTRODUCTION

Peroxy radicals (RO2) are formed in the atmospheric oxidation of VOCs. In the atmosphere, the RO2 radicals are often assumed to react with NO, HO2 and other peroxy radicals, and to lesser extent with NO3. RO2 radicals are also formed in the low-temperature combustion of VOCs, where they undergo intramolecular H-migration as RO2 → QOOH → Products. Because of the high endothermicity and high barriers, the H-migration is often excluded in the atmospheric oxidation mechanism of VOCs. In the past few years, both experimental and theoretical studies showed that the H-migration in the peroxy radicals might be important in the oxidation of biogenic hydrocarbons. (Ehn et al., 2014; Jokinen et al., 2014; Rissanen et al., 2014; Peeters et al., 2014; Berndt et al., 2016) However, little research has focused on this behavior in anthropogenic organic compounds. (Crounse et al., 2013; Jørgensen et al., 2015) Here we report our recent studies on the role of intramolecular H-migrations in the atmospheric oxidation of certain types of anthropogenic compounds, including ethers (Wang et al., 2016), substituted benzenes, and carbonyl compounds. These kind of unimolecular reactions might be fast enough to compete with bimolecular reactions in the urban atmosphere, and may result in formation of highly oxidized multifunctional compounds (HOMs) and contribute to SOA formation. Moreover, the importance of H-migrations would significantly increase with elevated temperatures, and some of the subsequent reaction channels might regenerate OH radical.

METHODS

All the molecular geometries are optimized using density functional theory at the M06-2X/6-311++G(2df,2p) level, and the electronic energies are calculated by using the complete basis set model chemistry with both unrestricted (UCSB-QB3) and restricted (ROCBS-QB3) wave function for the open-shell species. In kinetics calculations, we have treated the internal rotations as uncoupled hindered rotors, and have obtained their potential energy profiles by fixing the corresponding dihedral angles with relaxing all other coordinates in optimization. Asymmetric Eckart model is used for the tunneling correction factors. The reaction rates/rate constants at high-pressure limit are estimated by transition state theory (TST):

\[ k = \sigma \cdot k_{B}T \cdot \frac{k_{B}T}{h} \cdot \exp \left( \frac{-\Delta G^*}{RT} \right) \cdot \left( \frac{RT}{P} \right)^{\frac{1}{2}} \cdot \left( \frac{N_{A}}{\ell} \right)^{-\frac{3}{2}} \cdot \left( E_1 \right) \]

For the pressure-dependence of the reaction kinetics, unimolecular rate theory coupled with the energy-grained master equation (RRKM-ME) is employed to estimate the effect of collision by using the
MESMER code. (Glowacki et al., 2012) Single exponential-down model is employed to approximate the collisional energy transfer. The collisional parameters are estimated by the method of Gilbert and Smith. We also carried out experiments to test intramolecular H-migrations and formation of highly oxidized products in the oxidation of alkylbenzenes. The experiments were performed in a free-jet flow system at a temperature of 295 ± 2 K, a pressure of 1 bar air and a reaction time of 7.9 s. The detection of highly oxidized RO₂ radicals and closed-shell products was carried out by means of CI-API-TOF (chemical ionization - atmospheric pressure interface-time-of-flight) mass spectrometry (Airmodus, Tofwerk, resolving power >3000 Th/Th) using acetate as the reagent ion.

CONCLUSIONS

We have predicted theoretically the occurrence of intramolecular H-migrations in certain types of peroxy radicals formed in the atmospheric oxidation of ethers, carbonyls and alkylbenzenes. The estimated rate coefficients vary from the order of 10⁻² s⁻¹ to 10¹ s⁻¹ with various substitute groups in different peroxy radicals (Table 1), which might be fast enough to compete with the bimolecular reactions of these peroxy radicals with NO and HO₂ or RO₂ radicals in the atmosphere. The predicted formation of highly oxidized multifunctional products in the oxidation of alkylbenzenes, through intramolecular H-migrations, is qualitatively supported by our experimental studies. This is shown for isopropylbenzene in Figure 1. To summarize, intramolecular H-migration can result in the formation of HOMs, which could contribute to the formation of SOA in urban areas. Moreover, recycling of OH radicals is proposed in certain cases, which may sustain the oxidizing power to the atmosphere. Therefore, we suggest that it is necessary to include the intramolecular H-migration of the RO₂ radical in the atmospheric oxidation mechanism of certain anthropogenic VOCs for air quality modelling.

Table 1. Reaction energies and barrier heights (ΔE_ref and ΔE_ref in kJ/mol) for the intramolecular H-migrations in the oxidation of ethers and carbonyls at UCBS-QB3 level; for alkylbenzenes at ROCBS-QB3 level; k_{H mig} in s⁻¹. T/EB/IB-R4-BPRs represent bicyclic peroxy radicals in toluene, ethylbenzene and isopropylbenzene, respectively, with OH additions to para-position.

<table>
<thead>
<tr>
<th>RO₂</th>
<th>ΔE_{NK}</th>
<th>ΔE_{ref}</th>
<th>k_{H mig}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂OCH₂O₂</td>
<td>39.5</td>
<td>85.7</td>
<td>7.4 × 10²</td>
</tr>
<tr>
<td>CH₂CH₂OCH₃CH₂O₂</td>
<td>37.2</td>
<td>75.1</td>
<td>1.6</td>
</tr>
<tr>
<td>(CH₃)₂CHOC(O₂)(CH₃)₂</td>
<td>39.3</td>
<td>69.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Carboxyls</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂C(O)O₂</td>
<td>24.3</td>
<td>97.5</td>
<td>9.13 × 10⁻³</td>
</tr>
<tr>
<td>CH₃CH₂CH₂C(O)O₂</td>
<td>10.8</td>
<td>83.6</td>
<td>3.34 × 10⁻³</td>
</tr>
<tr>
<td>(CH₃)₂CHCH₂C(O)O₂</td>
<td>6.1</td>
<td>67.5</td>
<td>6.81 × 10⁻¹</td>
</tr>
<tr>
<td>Alkylbenzenes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-R4-BPR</td>
<td>12.5</td>
<td>93.2</td>
<td>2.6 × 10²</td>
</tr>
<tr>
<td>EB-R4-BPR</td>
<td>-3.9</td>
<td>76.8</td>
<td>7.0</td>
</tr>
<tr>
<td>IB-R4-BPR</td>
<td>-5.5</td>
<td>69.8</td>
<td>14</td>
</tr>
</tbody>
</table>
**Figure 1.** Mass spectra recorded from the reaction of OH radicals with isopropylbenzene, IB. The red spectrum represents the background measured in absence of isopropylbenzene. Products are detected as adduct with acetate. The spectrum depicted in part A was measured in absence of NO and that in part B with a NO concentration of $5 \times 10^{13}$ molecules cm$^{-3}$. Reactant concentrations (unit: molecules cm$^{-3}$): [O$_3$] = $6.6 \times 10^{13}$, [TME] = $1.0 \times 10^{13}$ and [isopropylbenzene] = $1.64 \times 10^{13}$.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


DETECTION OF HO$_2$ AND CYCLOHEXENE OZONOLYSIS RADICALS AND PRODUCTS BY AN IODIDE-CIMS

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Keywords: HO$_2$, PEROXY RADICAL, CHEMICAL IONIZATION, IODIDE.

INTRODUCTION

The HO$_2$ radical plays a critical role in the lifetimes of peroxy radicals in the atmosphere. The propensity of the precursor peroxy radicals formed through the ozonolysis of biogenic VOCs to autoxidate and produce low-volatile highly oxygenated molecules (HOMs) has been investigated previously (Rissanen, 2014). In addition, the kinetics of the radical sink RO$_2$ + HO$_2$ bimolecular reactions have been well studied (Hasson, 2012). The RO$_2$ + HO$_2$ → ROOH + O$_2$ pathway, for example, is a radical sink process in the atmosphere, that leads to the formation of stable products. An experimental method that can simultaneously detect the HO$_2$ radical, peroxy radicals and the products of the reaction between the two would help understand the fate of peroxy radicals in the atmosphere. In this work, through computational and experimental investigations, we present the direct detection of the HO$_2$ radical using an iodide-based chemical ionization mass spectrometer (iodide-CIMS). This is followed by the detection of a set of peroxy radicals and closed-shell molecules produced from cyclohexene ozonolysis. The dimerization of peroxy radicals via the RO$_2$ + RO$_2$ pathway was also probed. Additionally, the mechanism for producing carboxylate ions via a dehydroxylation reaction by the I$^-$ reagent ion in the presence of water was computationally established.

METHODS

Computational calculations to extract molecular enthalpies were performed at the PBE/aug-cc-pVTZ-PP level for the radicals and at the DLPNO-CCSD(T)/def2-QZVPP//PBE/aug-cc-pVTZ-PP level for the closed-shell molecules. An iodide-CIMS with an ambient pressure ion molecule reaction region (IMR) was used for the experimental detection. The HO$_2$ radical was produced by photolyzing water with a 184.9 nm UV lamp in the presence of oxygen. The peroxy radicals were produced by adding cyclohexene, ozone and oxygen into the system and allowing them to interact in a 2-meter long flow tube.

CONCLUSIONS

Calculations showed that the HO$_2$$^*$I$^-$ cluster had a binding enthalpy of 21.6 kcal/mol. Refering to the previously established relation between iodide-molecule cluster binding enthalpies and iodide-CIMS instrument sensitivities, the predicted sensitivity of an iodide-CIMS for the HO$_2$ radical was found to be 0.40 cps/ppt (Iyer, 2016). This was followed by an experimental investigation using an iodide-CIMS that resulted in the successful detection of the HO$_2$$^*$I$^-$ cluster at 159.9027 Th. Fig. 1 shows the optimized HO$_2$$^*$I$^-$ cluster and the iodide-CIMS mass spectrum with the corresponding peak. The RO$_2$ radicals that were investigated in this paper were C$_6$H$_9$O$_{4-8}$, which are
the initial peroxy radical and the subsequent two autoxidation products of cyclohexene ozonolysis (Rissanen, 2014). The time-series during the measurement sequence of these peroxy radicals and their closed-shell ROOH forms after the bimolecular reaction with HO₂ are shown in Fig. 2. The iodide-CIMS also detected peaks corresponding to possible dimers and carboxylate ions formed via dehydroxylation reactions between I⁻ and peroxy acids.

Figure 1: a) Optimized HO₂⁺I⁻ cluster at PBE/aug-cc-pVTZ-PP level. b) Iodide-CIMS spectrum with the visible HO₂⁺I⁻ peak at mass/charge 159.9027. Inset: HO₂⁺I⁻ peak.

Figure 2: Time series of selected radicals and closed-shell products during the experiment with half minute signal averaging time.

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REFERENCES


ANTHROPOGENIC AND BIOGENIC VOC FLUXES FROM A BOREAL FOREST IN SOUTH FINLAND

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Keywords: PTR-TOF, eddy covariance, exchange, flux, butanol.

INTRODUCTION

Boreal forests cover a vast area on our planet and their emissions have an important impact to the air quality and air chemistry of the northern atmosphere. This exchange between biosphere and atmosphere is dominated by water vapor and CO2. In much lower amounts, various volatile organic compounds (VOCs) are emitted, which are used in plant communication, as protection against stresses (e.g. O3, heat, herbivores) or are a by-product of the plant metabolism (Mogensen, 2015 and references therein). These emissions can lead to aerosol formation and the growth of aerosols to form cloud condensation nuclei and later on cloud droplets, which can influence the global climate. At the station for measuring ecosystem-atmosphere relations II (SMEAR II) instruments measure all those parameters and relations are investigated.

METHODS

The measurements took place between April and June 2013 in SMEAR II. The station is located in a forest consisting mainly of Scots pines (Pinus sylvestris) and Norway spruces (Picea abies). The VOC

![Diagram showing composition of emissions]
exchange was measured using a proton transfer reaction time of flight (PTR-TOF) mass spectrometer. This instrument is capable of measuring full VOC spectra in a 10 Hz time resolution, therefore it was possible to use eddy covariance (EC) method, a direct technique for determining ecosystem exchange.

RESULTS

In Fig. 1 the composition of the emissions of April (left) and June (right) are shown. The compounds with flux drastically increased from early spring (3) to summer (17). Also the net VOC flux showed a similar pattern, as in April it reached 0.66 nmol m\(^{-2}\) s\(^{-1}\), while in June it went up to 3.00 nmol m\(^{-2}\) s\(^{-1}\). Almost 2/3 of the emissions in April were from butene, followed by emissions from monoterpenes and acetone. In June the picture changes, as methanol dominated with almost 40% of the total emissions. Similar as in April, second and third most emitted compounds are the monoterpenes and acetone. In June the monoterpenes have a higher flux than acetone, however. In fourth position is butene, which only contributes with 8%. Acetic acid is the last compound, which has a higher contribution than 5% to the net flux, the remaining 11 compounds amount in sum to 13% of the emissions.

The butene emissions were interesting, as they were strongly emitted in April, when the temperature and the photosynthetically active radiation (PAR) were low. Furthermore, in the warmer and PAR richer June the absolute emissions even decreased. Identifying the source proved difficult, as butene can be emitted biogenically (e.g. Hakola et al., 1998), anthropogenically (e.g. Na et al., 2004), or can be a fragment of butanol (Denzer et al., 2014). Therefore the fluxes were divided into wind sectors and the average flux for each direction was calculated. In Fig. 2 the result is shown for June 2013. The very asymmetric behavior rejects a biogenic source, as the forest surrounding the measurement cottage is quite homogeneous. But in the direction of the butene emissions were the particle measurements of SMEAR II (orange circles). A fragmentation test with butanol used at the measurement side showed that the most prominent signal is on the butene mass. Therefore, we assume that the measured butene flux was anthropogenic, created by evaporating butanol from the condensation particle counters.

Figure 2: Average butene emission from wind direction sectors are shown in yellow, while orange circles mark the position of particle counters. The map was taken from google maps (Imagenary©2016 Google, Map data©2016 Google).
CONCLUSIONS

The VOC exchange measurements at SMEAR II showed a high diversity. The majority of the fluxes increase from April to June. Overall 25 different VOCs had emissions, 12 showed exchange just in one month only. The major biogenic fluxes originated from the monoterpenes and acetone and during the growing season methanol. The butene fluxes are most likely a fragment of butanol, which is used in particle measurements at the station. The fluxes are not very dependent on ambient temperature or PAR as they are evaporated from the air conditioned measurement cottages.

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REFERENCES


MEASUREMENT OF GAS PHASE IODINE-CONTAINING COMPOUNDS

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Keywords: CI-API-TOF, IODINE, HIO₃.

INTRODUCTION

Homogeneous nucleation via HIO₃ addition has been discovered to be an important source of iodine-containing particles at Mace Head (Sipilä et al., 2016). The chemistry mechanism behind the formation of HIO₃ has only been calculated by quantum mechanism (Drougas & Kosmas, 2005; Plane et al., 2006). However, no dedicated experiments were conducted to confirm the mechanisms. In this work, we present a chemical ionization mass spectrometry method which has the potential to detect a series of gas phase iodine-containing compounds. We will also propose the formation mechanism of HIO₃.

METHODS

A nitrate ion-based (Jokinen et al., 2012) and an iodide-based (Iyer et al., 2016; Lee et al., 2014) chemical ionization atmospheric pressure interface time of flight mass spectrometer (CI-API-TOF) were installed in our laboratory to measure gas phase iodine-containing compounds. A well-controlled flow tube was employed to study the formation mechanism of HIO₃.

CONCLUSIONS

Nitrate ion-based CI-API-TOF has shown its ability to detect HIO₃ at Mace Head. Our field campaigns also suggest the existence of HIO₃ in other locations, such as a boreal forest (SMEAR II station, Hyytiälä), Greenland and Antarctica. In our recent laboratory experiments, multiple pathways leading to the formation of HIO₃ have been found. The employment of an iodide ion-based chemical ionization method extended our capability to detect more gas phase iodine-containing compounds, including HIO₃, HIO₂, HIO, IO, IO₂, I₂O₂, I₂O₃, I₂O₄, HO, INO,INO₂, INO₃, I, I₂. This method awakens a potential way to comprehensively study the radical reactions between gas phase iodine-containing compounds.

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REFERENCES


HETEROGENEOUS NUCLEATION OF NaCl DIHYDRATE IN SUPERCOOLED DROPLETS OF SEA SALT ANALOG SOLUTION

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Keywords: Sea salt aerosol, heterogeneous nucleation, sodium chloride dihydrate, Raman spectroscopy

INTRODUCTION

Seawater spray is the dominant source of atmospheric aerosol over oceans and in coastal areas. With its global emission of 1733 Tg/y the sea spray aerosol (SSA) compares only with mineral dust (Koch, 2006). The phase state of sea spray particles controls their physical and chemical properties, for example, in interaction with ozone (Koop, 2000) or in heterogeneous nucleation of ice (Wise, 2012; Wagner, 2013). The NaCl aerosol can exist either as aqueous solution droplets or in one of the two crystalline forms: anhydrous NaCl and NaCl dihydrate (NaCl·2H₂O). The latter can serve as an efficient ice nucleating particle and is essential for the microphysics of high altitude marine clouds (Wise, 2012; Schill, 2014). The nucleation of NaCl dihydrate in sea spray aerosol may be further influenced by the presence of inorganic (CaSO₄, MgCl₂, MgSO₄, KMgCl₃) and organic substances. Some of these salts (e.g., gypsum or bassanite) have lower solubility than NaCl and therefore would precipitate at humidity values higher than ERH of crystalline NaCl (Tang, 1997; Koop, 2000; Xiao, 2008; Wise, 2009). Precipitated salts could facilitate heterogeneous nucleation of hydrated NaCl. However, reliable prediction of effloresced fraction as a function of temperature was impossible due to the absence of experimental data on key parameters such as solid-liquid interfacial energy or diffusivities of water and ionic species in the low temperature range.

Here we report the measurements of nucleation rate coefficient of NaCl dihydrate in the aqueous solution droplets of pure NaCl and sea salt analogue (SSA) solution suspended in an electrodynamic balance (EDB) (Peckhaus, 2016). We have derived the interfacial energy of crystalline NaCl dihydrate in a supersaturated NaCl solution in the temperature range from 240 to 250 K. With this data, we have applied a heterogeneous classical nucleation theory (CNT) model to explain the high temperature shift of the NaCl dihydrate efflorescence for SSA droplets, assuming the presence of super-micron solid inclusions (hydrate or hemihydrate of CaSO₄). Scanning Electron Microscope (SEM) and energy dispersive X-ray analysis of individual aerosol particles collected in the cloud chamber has confirmed the presence of such inclusions.

MATERIALS AND METHODS

We have used a humidity controlled electrodynamic balance coupled to the inverted Raman Microscope (Peckhaus, 2016). The relative humidity (RH) inside the EDB has been set between 38% and 44%. The time between injection and efflorescence of NaCl solution droplets has been recorded for every efflorescence event, allowing for determination of volume specific nucleation rate. After the efflorescence, both Raman spectra and optical images have been recorded allowing for the detection of particle phase and morphology. In total, we have studied over 600 NaCl solution droplets and over 250 sea salt analogue droplets. The homogeneous nucleation rate coefficient of NaCl dihydrate was measured for 5 different temperatures between 240 and 250 K by plotting the fraction of effloresced particles as a function of time and accounting for concentration change in the evaporating droplets (Peckhaus, 2016).

An environmental scanning electron microscope (ESEM FEI, Quanta 650 FEG) equipped with the energy dispersive X-ray (EDX) spectrometer (Bruker) have been used to record images and chemical maps of individual SSA particles deposited on a silicon wafer. The particles for the ESEM study have been produced by depositing droplets of sea salt analogue solution (Instant Ocean®) onto a silicon wafer and allowing them to evaporate at room conditions. Atlantic sea salt particles have been sampled from the cloud chamber AIDA on the Nuclepore membrane filters with the pore diameter of 200 nm.
EXPERIMENTAL RESULTS AND CNT-BASED PARAMETERIZATION

The Raman spectra of the SSA solution droplets and residual particles have been used to identify the NaCl phase after efflorescence (Fig. 1). The spectral features used for identification of crystalline phase of NaCl were the two sharp peaks corresponding to the stretching vibrations of water at 3424 cm⁻¹ and 3545 cm⁻¹, and the librational mode at 390 cm⁻¹. These features are unique for NaCl · 2H₂O, and, if present, always dominate the Raman spectrum in this region due to the prevalence of NaCl in the solution Wise (2012). The hydrated salts other than NaCl could be identified based on their own characteristic H₂O stretching and bending modes. For example, the spectrum shown in black in the Figure 4 is characteristic for carnallite (K₂MgCl₂ · 6H₂O), found previously in SSA particles (Xiao, 2008). All Raman spectra of SSA particles contained the ν₁(SO₄²⁻) stretching mode peak at 984 cm⁻¹ and an additional minor feature at 1008 cm⁻¹ indicating the presence of aqueous SO₄²⁻ ions in the environment of Ca²⁺ and Mg²⁺ ions (Zhang, 2000). The Raman spectra clearly show that even after efflorescence a significant amount of hydration water is present in the SSA residual particles (Tang, 1997).

The ESEM / EDX study of residual SSA particles deposited onto a Si wafer revealed their complex morphology and chemical composition. SSA particles contained clearly recognizable cubic crystals of anhydrous NaCl embedded into the crust of other inorganic components (Fig. 2).

**Figure 1.** Raman spectra of the suspended SSA solution droplet (green), SSA residual particles containing NaCl · 2H₂O (red), residual particle containing NaCl and precipitated carnallite K₂MgCl₂ · 6H₂O (black), and residual particle containing precipitated anhydrous NaCl in the presence of dissolved ionic species (blue). The spectra are normalized to the sulfate stretching mode peak at 984 cm⁻¹ and are vertically offset for clarity.

**Figure 2.** ESEM and shadow images of sea salt residual particles. **Left panel:** Atlantic sea salt residual particle sampled from the cloud chamber AIDA on the Nuclepore membrane filter. Note the needle-like bassanite CaSO₄ · 0.5H₂O crystals. **Middle panel:** ESEM image of SSA residual particle overlaid with the EDX color map of Ca, Mg, and S. **Right panel:** Shadow images of (A) anhydrous NaCl, (B) NaCl dihydrate, (C) SSA particles containing anhydrous NaCl, and (D) SSA particles containing NaCl dihydrate. The scale bars in the right panel are 20 μm.
The EDX mapping of this crust revealed that Ca, S, and O were co-located (see Fig. 2, middle panel), suggesting formation of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ (gypsum) or $\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$ (bassanite), which can be part of a gypsum formation pathway (Wang, 2012). Both gypsum and bassanite have solubility values lower than that of NaCl, implying that they should precipitate prior to the efflorescence water activity of NaCl dihydrate is reached. We argue that these precipitated salts serve as centers of heterogeneous nucleation of NaCl dihydrate.

The total volume specific homogeneous nucleation rate for NaCl dihydrate in the pure NaCl droplets has been determined from the time resolved efflorescence measurements (Fig. 3, left). It shows that the homogeneous nucleation rate coefficient of NaCl dihydrate increases with decreasing temperature, while the total nucleation rate does not show temperature dependence in the investigated temperature range. These measurements allowed us to derive the interfacial energy of the NaCl dihydrate crystal in the supersaturated NaCl solution. Based on this data and also using the parameterization of water diffusivity in concentrated NaCl solution based on the data of Garbacz (2014) and Koop (2016), we have constructed a CNT model of the NaCl dihydrate nucleation taking into account the temperature and concentration dependence of the volume specific nucleation rate. This model adequately describes our experimental data and the data previously obtained by Wagner (2012) and Wise (2012), for details see Peckhaus (2016).

The temperature-dependent formation of NaCl dihydrate in sea salt analogue solution droplets is shown in Fig. 3, right panel. The efflorescence curve is shifted to higher temperatures by approximately 5.5 K compared to the pure NaCl case. We suggest that heterogeneous nucleation of NaCl dihydrate might be responsible for the enhanced formation of NaCl dihydrate in SSA solution droplets. The fraction of NaCl dihydrate forming via heterogeneous nucleation has been calculated as:

$$f_{\text{het}}(T) = 1 - \exp(-J_{\text{het}}(T) \cdot s_{\text{incl}} \cdot t)$$ (1)

where $s_{\text{incl}}$ is the surface area of a solid inclusion and $J_{\text{het}}(T)$ is the heterogeneous nucleation rate coefficient calculated with account for the reduced energy of the critical nucleus formation. Note that $f_{\text{het}}(T)$ does not depend on the droplet size but only on the size of inclusion.

**Figure 3. Left panel:** Volume specific nucleation rates of NaCl dihydrate calculated from efflorescence experiment. **Right panel:** Fraction of NaCl dihydrate in SSA particles and the CNT-based parametrization of heterogeneous nucleation of NaCl dihydrate in SSA droplets (the solid black line and the shaded area). Experimental data and the CNT parametrization of heterogeneous nucleation of NaCl dihydrate in NaCl solution droplets are given in diamonds and black dashed line respectively.

The CNT-based model for NaCl dihydrate is shown as the solid black line in Figure 3, right panel. We calculate the fractions of precipitated NaCl dihydrate as a function of temperature assuming the size of an inclusion $d_{\text{incl}} = 3 \mu m$ but otherwise keeping all experimental parameters as in the case of pure NaCl solution. The calculated curve adequately reproduces the measurement data. By allowing a variability of inclusion size within $(3 \pm 1) \mu m$ the spread of the experimental data can be covered as well (the grey shaded area in Figure 3, right panel). The chosen size of inclusion roughly corresponds to the mass fraction of $\text{CaSO}_4$ in the Instant Ocean® sea salt analogue mixture, under assumption that all $\text{CaSO}_4$ in a droplet precipitates into a single spherical particle.
CONCLUSIONS
We report series of single droplet efflorescence experiments with micron-sized droplets of NaCl and sea salt analogue (Instant Ocean®) solutions suspended in the EDB at constant temperature and humidity. Our motivation was to establish a relationship between the crystalline phase of the effloresced particle and the thermodynamic and kinetic conditions of a solution droplet. The temperature-dependent partitioning between anhydrous NaCl and NaCl dihydrate has been observed in the temperature range from 240 K to 250 K, with NaCl dihydrate mostly forming at lower temperatures. Our experimental results are in a good agreement with the data of Wise et al. (2012) but differ from the observations of Wagner et al. (2012) where a strong increase in dihydrate formation was observed at temperatures below 235 K. Using our nucleation rate measurements and parameterization of water diffusivity of Garbacz (2014), we have constructed a CNT model of the NaCl dihydrate nucleation that has resolved this apparent inconsistency.

Following the concept of heterogeneous nucleation, the CNT model was adjusted to account for the presence of solid inclusions in natural seawater droplets and in SSA solution droplets. These inclusions, presumably being inorganic salts of lower solubility, are capable of catalyzing the nucleation of NaCl dihydrate at lower concentration and / or higher temperatures, or shorter induction times. Assuming the presence of such super-micron inclusions, our model was able to predict the 5 K shift of dihydrate efflorescence curve towards higher temperatures observed for the SSA solution droplets. An electron microscope analysis of droplet residuals revealed the presence of CaSO4·2H2O (gypsum) or CaSO4·0.5H2O (bassanite) crystals, potentially responsible for the enhanced nucleation rate of NaCl dihydrate.

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REFERENCES
Observing the mixing layer with Doppler lidar

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Keywords: lidar, doppler, layer.

INTRODUCTION

Better understanding of the processes occurring within the boundary layer is essential in many aerosol studies as well as for improving the modeling of the developing and decaying of the boundary layer. Regional as well as global models can model the boundary layer reasonably well when considering longer time scales and statistics. However, more thorough of the modeling boundary layer could still be improved greatly. The work carried out in this study will show that the boundary layer can be classified into states based on the drivers causing the mixing. This will lead to a wider understanding which parts of the atmospheric profile are connected to the surface. In addition, different weather forecast and climate models require different input parameters on the low level winds and turbulence. Another goal is to provide parameters, which are obtained with Doppler wind lidar (Pearson et al., 2009, Hirsikko et al., 2014, Manninen et al., 2016), that can be used as inputs by the different models.

METHODS

The method utilizes a scanning Doppler Wind lidar instrument and a combination of measurements such as: attenuated backscatter coefficients, vertical velocity skewness, turbulent kinetic energy dissipation rate (O’Connor et al., 2010), vector wind shear, and relative signal to noise variance. In addition, the sonic anemometer measurements, which uses standard eddy covariance methods, if available can be used to include extra information of the state of the boundary layer.

Figure 1. Different lidar product that are used in identification of the source of mixing measured on April 2013 at Juelich, Germany.
CONCLUSIONS

The preliminary show that the method works well and can be applied routinely for clear-sky cases. There is still plenty of possible additions and fine tuning to perform. Also, classification for day with precipitation needs improvements. Future work will focus on further developing the method and reducing the uncertainties.

![Figure 1. An example of a classification on April 2013 at Juelich, Germany.](image)

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REFERENCES


STUDYING AEROSOL RADIATION FEEDBACK LOOP BASED ON SATELITE DATA

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INTRODUCTION

Apart from having an important role in defining air quality, atmospheric aerosols are found to affect the Earth’s radiation budget directly by scattering and absorbing incoming solar radiation and indirectly by changing cloud properties (IPCC 2013). All these impacts are largely affected by the size of the aerosol particles. Thus, studying the parameters involved in the formation and growth of atmospheric particles is essential for understanding their role in our atmosphere. New particle formation (NPF) is found to contribute to at least 50% of the cloud condensation nuclei (CCN) count globally (Merikanto et al. 2009; Kerminen et al. 2012). Freshly-formed clusters are born with diameters of smaller than 2 nm, and they further grow via condensation of available vapors to reach sizes where they can affectively act in modifying atmospheric properties (Dal Maso 2005).

For instance, in order to act as CCN, freshly-formed particles need to grow to a diameter of at least 50 nm and in order to effectively scatter solar radiation, particles need to reach a diameter of 100 nm (Sundström et al. 2015). Sulfuric acid has been found to contribute to the NPF and growth of atmospheric particles. Additionally, oxidation products of biogenic volatile organic compounds (BVOCs) are involved in NPF as well as in the growth of particles formed by NPF (Ehn et al. 2014). Thus, plant processes, photosynthesis in particular, play an important role in atmospheric NPF and growth phenomena (Mäkelä et al. 1997 and Kulmala et al. 2014). Therefore, the growth rate (GR) due to vapor condensation is important for determining the biosphere-aerosol-cloud-climate (COBACC) feedback mechanisms (Kulmala et al. 2014).

In order to estimate the regional effects of condensation growth, we need to first estimate the concentrations of the vapors involved in this process as well as the spatial distribution of aerosols. For this purpose, satellite measurements would be suitable tools to adopt as they provide information about the spatial distribution of aerosols and trace gases (Sundström et al, 2015), as well as the vegetation structure and photosynthesis, which may be applied in estimating BVOC concentration and eventually the GR by condensation (Nichol et al. 2000 and Kulmala et al, 2014). In this study, our aim is to study the aerosol radiation feedback based on satellite data in semi-clean boreal forest in southern Finland.

METHODS

The ground based data that we use in our analysis was obtained from SMEAR (Station for Measurement of Ecosystem-Atmosphere Relations) II measurement station located in Hyrylä, southern Finland (Hari and Kulmala, 2005). A boreal forest surrounds this station, and major pollution sources are located far away. Long-term measurements of aerosol particle number size distribution are available in this station as well as meteorological quantities such as ecosystem measures.
We focused on cloud-free conditions to diminish the effect of clouds (Kulmala et al, 2014). We used included data with the cloudiness parameter greater than 0.85 in our study.

We used several quantities obtained from ground-based measurements that are (presumably) related to the aerosol radiation feedback, and tried to find reasonable satellite retrievals for them. Gross primary production (GPP), which is a measure of eco-system-scale photosynthesis, was derived from the net ecosystem exchange, primary flux measurement during 1997-2016 (Kulmala et al, 2014). The condensation sink, describing the rate condensable vapors are removed from the atmosphere due to their condensation to aerosol particles (Kulmala et al. 2014), was calculated from DMPS measurements. The ambient temperature (T) as well as Global Radiation (0.30 – 4.8 µ) are measured by a mast level of 18 m above canopy. The measurement station also combines different measurements of trace gas concentrations, which might also be later included in our study.

Remote sensing of vegetation by using broad band sensors of vegetation offers vegetation cover indices, such as the normalized difference vegetation index (NDVI) (Tucker, 1979). This index will be used in this study as it correlates well with fraction of photosynthetically active radiation (0.4-0.7 µm) absorbed by the vegetation (FAPAR) (Ranga et al.1997 and Nichol et al. 2000).

The overall plan for data analysis is presented in Fig. 1.

![Data acquisition diagram](https://example.com/data-diagram.png)

**Figure 1.** Data acquisition diagram. Straight lines are direct calculations while skewed arrows are there to explain the data that will be used in forming our proxy.

**DISCUSSION AND OUTLOOK**

To study aerosol radiation feedback based on satellite data, we need to investigate the connections between BVOC emissions, photosynthesis (GPP), and aerosol properties such as condensation sink, considering also temperature changes.
As seen from Fig. 1, for achieving our aim of analyzing aerosol radiation feedback loop, temperature and aerosol properties from satellite data will be used. In addition, NDVI/fluorescence offers information about GPP and it provides the necessary estimates for BVOC concentrations.

Validation of our satellite-based studying will be made by comparing it to the ground-based measured data. For instance, the relation of ratio between diffuse radiation and global radiation with temperature in the boundary layer was studied here.

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REFERENCES


AEROSOL OPTICAL PROPERTIES DURING A POLLUTED WINTER PERIOD AT SORPES, A REGIONAL BACKGROUND STATION IN NANJING, CHINA

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Keywords: SCATTERING, ABSORPTION, TRAJECTORY CLUSTERS.

INTRODUCTION

Long-term continuous measurements of aerosol optical properties (AOPs), particle size distributions, aerosol chemical composition and other relevant parameters including trace gas concentrations and meteorological parameters are conducted at the Station for Observing Regional Processes of the Earth System (SORPES), a regional background station in Nanjing, China. The site is located in the Yangtze River Delta (YRD), one of the most industrialized and polluted regions in China. In this study, we present four months of AOP observations and an analysis of their temporal variations, relationships with particle size distributions and transport. Ding et al. (2016) and Petäjä et al. (2016) analyzed the interactions of pollutants and the planetary boundary layer (PBL). They showed that high PM and especially BC concentrations enhance the stability of a polluted boundary layer by modifying the PBL temperature profile and by decreasing the surface heat flux. In these papers observational data from SORPES were used but there was no detailed analysis of how particle size distributions and AOPs evolve during extreme haze pollution episodes. Such an analysis is presented in this work.

METHODS

The scattering and backscattering coefficients were measured at three wavelengths (λ = 450, 525 and 635 nm) using an integrating nephelometer (Aurora 3000, Ecotech). Light absorption was measured using a 7-wavelength aethalometer (AE-31, Magee Scientific) at λ=370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm, and 950 nm. Particle number size distributions were measured using a custom-made Differential Mobility Particle Sizer (DMPS) in the size range of 6 – 800 nm. The number size distributions were used here for estimating mass concentrations of particles smaller than 800 nm and for calculating effective diameters. Particle chemical composition, the mass concentration of particles smaller than 2.5 µm (PM2.5), trace gas concentration, and meteorological parameters were measured simultaneously at the same site.

The HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model version 4.9 driven with Global Data Assimilation System (GDAS) output was used to do cluster analysis of backtrajectories.

RESULTS AND DISCUSSION

The time series of several extensive and intensive aerosol properties from 1 November 2013 to 28 February 2014 are presented together with the modeled planetary boundary layer height (PBLH) in Figure 1. In addition, the time series of the trajectory cluster classes are presented as the background shading colors.
Figure 1. Aerosol optical properties, mass concentrations and modeled boundary layer height during a polluted 4-month period from 1 November 2013 to 28 February 2014. PBLH: Planetary Boundary Layer Height; PM$_{2.5}$ and PM$_{1}$: mass concentration of particles in the aerodynamic particle diameter ranges D$_{p} < 2.5$ μm and D$_{p} < 1$ μm; BC: Black Carbon mass concentration; GMD: geometric mean diameter of particle number size distribution; σ$_{sp}$ and σ$_{ap}$: scattering and absorption coefficient at λ = 525 nm; MSE: mass scattering efficiency at λ = 525 nm; SAE and AAE: Ångström exponents of scattering and absorption; SSA: single-scattering albedo at λ = 525 nm; b: backscatter fraction at λ 525 nm; AF/σ: radiative forcing efficiency at λ = 525 nm.

It is possible count approximately 14 – 16 distinguishable pollution episodes by using either the PM concentration or the scattering coefficient time series. The analyzed period was 120 days long so on the average there was a pollution episode about every 8 ± 1 days. The definition of the start and end of a pollution episode is not unambiguous, however, so the above number should be treated cautiously.
The trajectory cluster time series, shown as the background shading colors in Figure 1, shows that when airmasses came from the WEST or from the YRD there were no big differences in concentrations. The COASTAL trajectory cluster was often but not always associated with lower concentrations. Most of the episodes ended with trajectories associated with the CLEAN cluster. Meteorological analyses show that the trajectories associated with the CLEAN cluster brought air from the north, high above Beijing during cold fronts. There were also episodes during which there were trajectories belonging to many different clusters, YRD, WEST and COASTAL but there were no clear differences in concentrations until the clearing phase associated with the cluster CLEAN. During these episodes polluted air arrived from all directions in line with wind roses that showed there was no strong dependence on wind direction. Instead, the concentrations kept rising.

Most episodes followed a similar pattern: during the evolution phase the concentrations grew day after day during several days at a rate of some tens of $\mu g \, m^{-3} / \text{day}$ but the end of the episode was usually abrupt, air cleared within hours. The largest drop in the period occurred on 2 – 3 February when PM concentrations and scattering and absorption coefficients decreased by more than an order of magnitude within hours. The same cycle applied to all extensive parameters: BC concentrations, absorption and scattering coefficients increased clearly more slowly during the growth phase of the episodes than decreased in the end. At the same time the daily maximum PBLH decreased during most of the episodes depicted in Figure 1. This PBLH decrease is in agreement with the analysis of Petäjä et al. (2016) and Ding et al. (2016) who showed that high PM and especially BC concentrations enhance the stability of a polluted boundary layer, which in turn decreases the boundary layer height and consequently cause a further increase in PM concentrations.

Even during the growing phase of the episodes there were obvious diurnal cycles of the AOPs. For instance, low PM concentrations, $\sigma_a$ and $\sigma_g$ during daytime and higher at night but still a growing trend can be explained with the formation of a residual layer: when the PBLH decreases at night part of the aerosol remains above the PBL. The following day new pollutants get mixed with the pollutants remaining in the residual layer. This leads to a continuous accumulation of aerosols in the PBL and a slower, non-symmetric cycle. The particle number size distribution time series shows that there are indications of new particle formation (NPF) also during the polluted period and that the new particles grew quickly into optically relevant size ranges and thus contributed to visibility reduction. Kulmala et al. (2016) estimated that about half of the particles in the accumulation mode, i.e., the optically relevant size range originate from NPF at SORPES even though the pollution level is high.

Also the intensive aerosol properties, i.e., those that do not depend on the amount of particles, clearly evolved during the pollution episode cycle. First, the effective particle size grew which is depicted as the time series of the geometric mean diameter GMD. There was an obvious diurnal cycle with the GMD as well. The Ångström exponents of scattering and absorption (SAE and AAE) as well as the backscatter fraction $b$ decreased as the particles grew. At the same time SSA increased which can be explained by condensation of light-scattering material and thus increasing the thickness of a shell surrounding a BC core. During the growth phase of the pollution episodes the radiative forcing efficiency (RFE = $\Delta F/r$) was almost constant. This is interesting since intuitively it could be thought that the higher SSA grows the lower is the RFE, in other words the more do the particles cool the atmosphere. That RFE remained fairly stable is due to the size of the particles: larger particles scatter light upwards less efficiently than small ones which to some extent compensates the higher SSA.

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REFERENCES


NEW PARTICLE FORMATION INSIDE THE EVOLVING BOUNDARY LAYER

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Keywords: ATMOSPHERIC BOUNDARY LAYER, CLUSTERS, NEW PARTICLE FORMATION.

INTRODUCTION

New particle formation (NPF) events frequently occur inside the continental boundary layer over the boreal forest region of Southern Finland (Kulmala \textit{et al.}, 2001, Kulmala \textit{et al.}, 2004, Kulmala \textit{et al.}, 2013). The phenomenon has been investigated near the ground level for over 20 years in the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations, Hari and Kulmala, 2005) field station in Hyytiälä, Finland.

Airborne measurements of aerosol particles have been conducted near the SMEAR II station (61°51'N, 24°17'E, 181 m above sea level) since the year 2003 using small aircraft (Laaksonen \textit{et al.}, 2008, O'Dowd \textit{et al.}, 2009, Schobesberger \textit{et al.}, 2013, Väätäinen \textit{et al.}, 2016) and hot-air balloons (Laakso \textit{et al.}, 2007, Petäjä \textit{et al.}, 2013). As a short overview, Laakso \textit{et al.} (2007) observed the new particle formation to occur in the mixed boundary layer but also in the free troposphere with no connection to the boundary layer nucleation. They used a hot-air balloon as a platform for particle and cluster measurements. O’Dowd \textit{et al.} (2009) observed the nucleation throughout the boundary layer over SMEAR II and the nucleation mode number concentration peaked above the forest canopy.

Schobesberger \textit{et al.} (2013) observed the new particle formation inside the planetary boundary layer. The highest concentrations of nucleation mode particles were found to be in the upper parts of the planetary boundary layer, which indicates that the nucleation does not necessarily occur only close to the surface. Väätäinen \textit{et al.} (2016) studied the vertical and horizontal extent of new particle formation in the lower troposphere near to SMEAR II station. They observed that the air masses within 30 km from SMEAR II only differed slightly from the ground-based observations at the station, though the variability of the differences was larger for the nucleation mode particles than for the larger particles. Furthermore, Väätäinen \textit{et al.} (2016) detected the nucleation to take place both inside the boundary layer as well as some times separately in the free troposphere.

In addition to near to surface nucleation inside the planetary boundary layer and free troposphere nucleation, another suggestion is that the nucleation takes place near the clouds (Wehner \textit{et al.}, 2015). Episodes of new-particle formation might take place also in elevated air layers that are not influenced by the surface, provided that the necessary gaseous precursors were transported there earlier.

Measurement techniques that enable detection of the smallest aerosol particles have developed during the last years. Total particle concentration can be measured with Condensation Particle Counters (CPC). A history of the CPCs is given in McMurry (2000). Aerosol particle size distributions can be measured by Pulse Height Condensation Particle Counter (PH-CPC) in the size range of 1.3 – 5 nm (Sipilä \textit{et al.}, 2008, Lehtipalo \textit{et al.}, 2009). The smallest ions and charged particles we can measure with Balanced Scanning Mobility Analyzer (BSMA) (in the size range of 0.8 – 7.5 nm) (Tammet, 2006) and Neutral Cluster and Air Ion Spectrometer (NAIS, Airel Ltd, Estonia, Manninen \textit{et al.}, 2009) (in the size range of 0.8 – 42 nm).
In addition to naturally charged particles, the NAIS measures also total particle distribution in the size range of 2 – 42 nm charging the neutral particles with a unipolar charger. One of the newest particle counters is the Particle Size Magnifier (PSM) which detects directly sub-3 nm atmospheric particles (Vanhanen et al., 2011).

In this work, we study the vertical distribution of the smallest clusters in the size range below 3 nm with a PSM onboard the Cessna aircraft. We have successfully measured small aerosol particles as small as 1.5 nm in diameter, as well as followed their growth and mixing in the evolving boundary layer using as small aircraft as the measurement platform.

METHODS

In this study, we have measured the total number concentrations of aerosol particles with a Particle Size Magnifier (PSM a10) (Vanhanen et al., 2011) including CPC TSI 3010 as a counter. The instrument had a 1.5 nm cut-off size determined in laboratory verifications. Total particle concentrations were measured with an ultrafine Condensation Particle Counter (uCPC, TSI 3776) that had a 3 nm cut-off size. The total particle number-size distributions were measured with a Scanning Mobility Particle Sizer (SMPS) in the size range of 10–400 nm. The instrument setup contained devices measuring meteorological parameters (pressure, relative humidity, temperature and wind), and concentrations of H2O and CO2 gases. This setup was used in two measurement campaigns: the first campaign was between May and June and the second was in August, in 2015.

The instruments were installed inside the cabin of a Cessna 172 airplane. The flights started from Tampere-Pirkkala airport. The flights were carried out above the SMEAR II station in Hyvölässä, Southern Finland with an altitude range of 300–3000 m above sea level. For detailed description of the instrumentation and sampling, see also Schöbesberger et al. (2013) and Väänänen et al. (2016).

RESULTS

During two measurement flights on Aug 13, 2015 we observed that the vertical profile of the cluster concentration (1.5 – 3 nm) was influenced by the boundary layer evolution and convection (Figure 1). The figure includes four measurement profiles from the ground level up to 2700 m above ground. The first two profiles were flown between 7:30 – 9:00 a.m. and the last two profiles between 10:45 a.m. – 12:45 p.m. The flights were performed around the SMEAR II station in Hyvölässä where the new particle formation event started around 10 a.m.

The small clusters were inside the mixed layer already before the event and they also extended into the residual layer during the first ascent. The mixed layer height was around 400 meters during the first profile and rose up to 1200 meters during the second profiles. During the second ascent and descent the NPF event was on-going and the cluster concentration increased throughout the boundary layer. In all the measurement profile figures we see that the total concentration measured by PSM was higher than the total concentration measured by uCPC inside the planetary boundary layer and about equal in higher altitudes. This indicates that the smallest clusters were not present above the mixed layer.

CONCLUSIONS

Based on the initial tests, we illustrated that the PSM can be operated as a part of aerosol instruments onboard an aircraft. Our results suggest that the clusters, which participate in new particle formation,
originate from near the forest canopy and their number concentration decreases as the altitude increases. The source near the surface is likely linked to the emissions from the vegetation. The decreasing concentration as a function of altitude is probably caused by vertical transport combined with limited cluster lifetime. A more detailed analysis is required to draw further conclusions on the vertical and spatial variability of the clusters.

Figure 1. Vertical profiles of total particle concentrations measured with PSM (green) with 1.5 nm cut-off size and ultrafine-CPC with 3 nm cut-off size (blue) on 13.8.2015 above the boreal forest site in Hyytiäliä. The first ascent and descent were flown at 7:30 – 9:00 a.m. and the last ascent and descent at 11:00 a.m. – 12:45 p.m.

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REFERENCES


HIGHLY-CONTROLLED, REPRODUCIBLE MEASUREMENTS OF AEROSOL EMISSIONS FROM BIOMASS COMBUSTION

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Keywords: BIOMASS BURNING, COMBUSTION, EMISSION FACTORS, BLACK CARBON, ORGANIC AEROSOL, LABORATORY MEASUREMENTS.

INTRODUCTION

Particulate emissions from biomass burning can alter the atmosphere’s radiative balance and cause significant harm to human health. Many of these emissions come from the residential burning of solid fuels, which is one of the greatest anthropological sources of black carbon worldwide (Bond et al. 2013). Biomass burning produces both black carbon and organic carbon in high quantities, which have opposing radiative impacts: the first predominantly absorbing and the second largely scattering incoming sunlight. It is therefore clear that emissions from the combustion of biomass must be well characterised in order for its impact on climate to be fully understood.

In atmospheric models, aerosol emissions from biomass burning are represented by emission factors or ratios based on mass loss or comparison with a reference gas, which are averaged over an entire combustion event for each particulate species. This approach, however, masks huge variability in emissions during different phases of the combustion period. Laboratory tests have shown that even small changes to the burning environment can lead to huge variations in observed aerosol emission factors (Akagi et al., 2011). Due to the largely chaotic nature of biomass combustion, it can be difficult to study the fundamental link between the immediate combustion behaviour and aerosol emissions in real-time.

In order to address this gap, in this study an emphasis was placed on enhancing the repeatability of combustion events in order to study fundamental effects on emissions as closely as possible, rather than attempting to simulate real-world combustion. This made it possible to observe changes in emissions as they occurred in real time over the course of eight combustion events, and the way in which these evolved during different phases of combustion.

METHODS

Combustion experiments were carried out using the FM Global Fire Propagation Apparatus (FPA) in the test facility at the School of Engineering, University of Edinburgh. The FPA allows small samples of fuel to be burned under highly-controlled conditions (Brohez et al., 2006). Samples within the FPA were surrounded by four infrared heat lamps, irradiating them evenly at either 30 kW m⁻² or 50 kW m⁻², and subject to incoming air from beneath at either 50 lpm or 200 lpm. The samples used were rubberwood (hevea brasiliensis), a variety commonly used in West Africa as a domestic cooking fuel, sourced from
Côte D’Ivoire. The samples were placed on a mass balance within the FPA in order to monitor mass loss. Exhaust from combustion was collected in a hood before entering into the exhaust tube. Air samples for measurement were extracted from a forward-facing inlet within the exhaust tube and diluted in pure nitrogen by a factor of 100. An Aerodyne Compact Time-of-Flight Aerosol Mass Spectrometer (AMS) was used to measure the concentration of organic aerosols and other non-refractory species. A Single Particle Soot Photometer (SP2) was used to measure the mass concentration of refractory black carbon (rBC). Both of these instruments are used regularly to measure ambient aerosol concentrations. Levels of CO₂, CO and O₂ in the exhaust gases were recorded with 1 Hz frequency.

Eight test burns were carried out during this experiment. Of these, two were carried out with the infrared heaters set to 30 kW m⁻² (low heat) and an incoming air flow rate of 200 lpm (high flow). Three were carried out with the heaters at 50 kW m⁻² (high heat) and a flow of 200 lpm (high flow). Three were carried out with the heaters at 50 kW m⁻² (high heat) and a flow rate of 50 lpm (low flow).

CONCLUSIONS

Figure 1 shows the time series of organic aerosol and refractory black carbon emitted during a test with the heaters at 30 kW m⁻² and a flow rate of 200 lpm. This has been chosen for illustrative purposes as it demonstrates most of the different emission behaviours seen throughout this experiment. Three clear phases can be seen in the emissions, which correlated closely with the phase of the combustion process taking place. Black carbon was emitted predominantly during flaming combustion (phase 2); organic aerosols during pyrolysis before ignition (phase 1) and from smouldering-dominated behaviour near the end of combustion (phase 3).

Figure 1. Particulate emissions of organic aerosol and black carbon during a test at 30 kW m⁻² with an airflow of 200 lpm. Three clear phases of combustion are indicated, corresponding to pre-ignition pyrolysis, flaming combustion and smouldering-dominated combustion.
During the flaming period, there was a strong correlation between the emission of black carbon and the rate of mass loss, which suggests there is value in employing a mass-based emission factor for this component. However, very little correlation was seen between organic aerosol and mass loss throughout the tests. As such, results here suggest that emission factors averaged over an entire combustion event are unlikely to be useful for organic aerosol emissions. The two different phases producing organic aerosol, pyrolysis and smouldering, were observed to have different mass spectra. In previous ambient experiments, two organic factors with very comparable signature to these have been identified using positive matrix factorisation (Young et al., 2015). As such, it is postulated that these ambient organic factors are likely associated with the two combustion phases identified here.

ACKNOWLEDGEMENTS

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REFERENCES


NEURAL NETWORK CLASSIFIER ON TIME SERIES FEATURES FOR PREDICTING ATMOSPHERIC PARTICLE FORMATION DAYS

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Keywords: Aerosol particles, Features, Neural network classifier.

INTRODUCTION

Atmospheric aerosol particles are minute molecular agglomerations suspended in the air. These small particles take part in a multitude of physical processes, some of which have very heavy societal impact: among these are the loss of visibility and harmful health effects — and even climatic consequences via aerosol-cloud interactions (Langridge et al., 2012). Atmospheric scientists are thus interested in understanding how various processes modify the properties of aerosol particles and especially how, why and when these particles form. However, the paths leading to atmospheric aerosol particle formation are not yet completely understood due to the vast physical and chemical complexity of the atmosphere. One straightforward approach to overcome this issue is to gather more data from the atmosphere.

Figure 1: Examples of non-event (a) and event (b) days at Hyyttiälä, Finland, in May 2005. Data accessed via Smart-SMEAR (Junninen et al., 2009).

Towards this end, several Stations for Measuring the forest Ecosystem-Atmosphere Relationships (SMEAR) have been established in Finland. These stations measure a large number of atmosphere
variables, such as gases, meteorology, radiation, aerosol particles and soil fluxes at different altitudes. At SMEAR II station in Hyytiälä forest alone (Hari and Kulmala, 2005), there are more than 260 observables in total since 1996 (i.e. millions in sample size), producing big data. The measurement of ambient aerosol size distributions is typically used to identify periods of new particle formation and growth (event days) and days when no particle formation is observed (non-event days). Figure 1 shows these two phenomena measured at Hyytiälä station. The x-axis shows the 24-hours time period whereas y-axis represents the range of particle diameters (from 3 nm to 1000 nm). The color indicates the particle concentration (cm$^{-3}$). Manual labor with such multi-years data for determination of event/non-event days is a challenging task and thus robust automated procedures for data analysis are called for (Kulmala et al., 2012). Here, we present a Machine Learning based neural network classifier to automatically determine atmospheric particle formation days.

**METHODOLOGY**

Aerosol particle concentration data from Differential Mobility Particle Sizer (DMPS) instrument is set to be the input to a Machine Learning model and its output is a list of event and non-event days based on expert visualization (Dal Maso et al., 2005). Figure 2 illustrates the block diagram of the proposed classification strategy. In the first step, the particle concentrations (at the range of 3nm-1000nm) are pre-processed to extract only useful data. In this step, we remove outlier data, which may contain suspicious data due to sensor fault or extreme conditions. Evening time periods for each day are also excluded because typically new-particle formation occurs during the day time (Hyvönen et al., 2005).

![Machine Learning classifier methodology used in this work.](image)

In the next step, we calculate two types of necessary features used in the analysis. Aerosol particle size distributions are fitted with a multi-modal Log-Gaussian distribution function using automatic algorithm developed by Hussein and coworkers (Hussein et al., 2005). The properties of the multi-modal Log-Gaussian distributions are taken as the first type of features. The second type of features are the time domain properties of particle concentrations, such as mean, standard deviation, kurtosis and skewness.

The combination of these features results in a large number of feature dimension which may lead to the *curse of dimensionality*: Machine Learning algorithms performing poorly with high-dimensional data (Bishop, 2006). This motivates the use of dimensionality reduction techniques, such as Principal Component Analysis (PCA). Thus, we project all of the obtained features using PCA onto Principal Components (PCs) space. We then extract only some of the highest variance PCs to be used as the inputs of the neural network classifier in the last step. As shown in Figure 3, we use a multilayer perceptron neural network with one hidden layer containing 25 neurons to perform classification (Hagan et al., 2014).
PRELIMINARY RESULTS AND CONCLUSIONS

We divide the data into two different parts: training and testing data. We use the data from 1996-2010 as training data whereas the period of 2011-2014 is used as testing data. The training data is fed into the neural network classifier for optimizing its weights. We use standard gradient descent optimization with regularization to avoid over-fitting during the training phase. The results of the training process are presented as a confusion matrix in Figure 4a. This metric presents the neural network accuracy over the manual visualization method (i.e. the target data set). It can be seen that the neural network training has a classification accuracy of 97.8%, indicating that the training process was very successful.

![Diagram of neural network classifier](image)

Figure 3: The structure of neural network classifier used in this work.

<table>
<thead>
<tr>
<th>Machine learning methods</th>
<th>Visualization methods</th>
<th>Event-day</th>
<th>Non-event days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event-day</td>
<td>1229</td>
<td>38</td>
<td>97%</td>
</tr>
<tr>
<td>42.2%</td>
<td>1.3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-event days</td>
<td>26</td>
<td>1621</td>
<td>98.4%</td>
</tr>
<tr>
<td>0.9%</td>
<td>55.6%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Training (1996-2010)

<table>
<thead>
<tr>
<th>Machine learning methods</th>
<th>Visualization methods</th>
<th>Event-day</th>
<th>Non-event days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event-day</td>
<td>251</td>
<td>75</td>
<td>77%</td>
</tr>
<tr>
<td>31.1%</td>
<td>9.3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-event days</td>
<td>59</td>
<td>423</td>
<td>87.8%</td>
</tr>
<tr>
<td>7.3%</td>
<td>52.4%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) Testing (2011-2014)

Figure 4: Confusion matrices of neural network classifier applied on training and testing data.

Once the training process is completed, the trained neural network classifier is then fed with testing data. The classification outcome is then compared with the target data set to evaluate the performance. These results are shown in Figure 4b. The method has a classification accuracy of 83.4% for determining event/non-event days using only aerosol particle concentration data from DMPS instrument. In other words, the neural network classifies automatically event/non-event days from 2011-2014 with the accuracy of 83.4%. In this case, the accuracy performance reduces from the training phase because the trained model may experience overfitting or the selected features might not represent well the particle concentrations needed for analysis.

Nevertheless, the proposed method seems promising and suggests that Machine Learning based methods might eventually solve this problem to higher accuracy. The presented method is to
be developed further by applying probabilistic models, such as Bayesian-based classifier, and by incorporating more measured variables into the scheme.

REFERENCES


Measurement of HOMs at two different heights: Influence of planetary boundary layer on HOM chemistry in the boreal forest

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Keywords: HOM CHEMISTRY, PLANETARY BOUNDARY LAYER, MASS SPECTROMETRY

INTRODUCTION

Highly oxidized multifunctional organic compounds (HOMs) have been suggested to play a critical role in new particle formation (NPF) and secondary organic aerosol (SOA) formation [Bianchi et al., 2016; Ehn et al., 2014; Kulmala et al., 2013; Riipinen et al., 2011], which have strong influence on global climate change and radiation budget [Hallquist et al., 2009; Merikanto et al., 2009]. It is recognized that HOMs are formed via the oxidation of volatile organic compounds (VOCs) but the exact HOM chemistry in the real atmosphere still remains poorly understood. On one hand, the roles of different groups of HOMs (e.g. HOMs with/without nitrogen) in NPF and SOA formation are complicated and may vary significantly. On the other hand, their formation pathways and fate are lack of investigation and may be altered with the changing environment conditions. Though HOMs measurements have been done in a few locations, the influence from planetary boundary layer (PBL) dynamics to HOM chemistry has been yet studied.

During the Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget (IBAIRN) campaign in Hyytiälä, Finland, HOMs were for the first time measured and compared at different heights with two nitrate ion based Chemical Ionization Atmospheric Pressure-interface Time-of-flight mass spectrometers (CI-API-TOF) [Jokinen et al., 2012], which offered us a good opportunity to investigate the PBL influence on HOM chemistry. Positive Matrix Factorization (PMF) model is also adopted in data analysis and the comparison of the HOMs measurements for both heights.

METHODS

Field measurements were performed at the boreal forest research station SMEAR II in Hyytiälä, southern Finland [Hari et al., 2013], during September 2016. The measurement tower is at 35m height above ground level and the canopy layer top is ~20m. During most of the nights, the tower top is above the PBL. Two nitrate ion based CI-API-TOFs were deployed on the ground and on the tower to measure the concentrations of HOMs and sulfuric acid. VOCs were measured with a proton transfer reaction time-of-flight mass
spectrometer (PTR-TOF-MS) [Graus et al., 2010] at ground level. The concentration and size distribution of particles and ions are observed also at different heights with a collection of instruments, such as particle size magnifiers (PSM), neutral cluster and air ion spectrometer (NAIS) and scanning mobility particle sizer (SMPS). Trace gas pollutants such as ozone (O₃), nitrogen oxides (NOₓ) and sulfur dioxide (SO₂) and meteorological parameters including relative humidity (RH), temperature, solar radiation, wind speed and wind direction were continuously monitored in 8 different heights from 4.2m to 125m (4.2m and 33.6m data are used in this study).

The algorithm and principle of PMF model used in this study is described in [Paatero and Tapper, 1994]. This model is based on the assumption of mass conservation and uses mass balance analysis to identify and trace the sources of the analysed measurement data. It is widely used in source apportionment on aerosol spectra because of its better treatment to data uncertainties and atmospheric relevant constrain solutions. Recently PMF model has been introduced in analysing unit mass resolution (UMR) data from CI-API-TOF mass spectrum, results indicated that PMF model could be a practical tool to examine the characteristics of HOMs [Yan et al., 2016].

CONCLUSIONS

During the campaign, difference between total HOM concentrations at ground-level and tower top were repeatedly observed during nighttime, accompanying with the rapid decrease of ground-level O₃ (see Figure 1). Examination of mass spectra from the CI-API-TOF indicated more nitrogen containing HOMs were formed in higher altitudes during nighttime, though the observed NOₓ concentrations were almost the same. This may either indicate the existence of strong NO₃ loss pathways, or ONs were fast depleted within the nocturnal PBL. No clear difference of HOMs was observed during daytime, suggesting the shift of PBL may have strong effect on HOMs formation and fate. Results from further analysis and PMF model will be presented in the meeting.

Figure 1. Time series of IBAIRN campaign Lines in red stand for the measurements at ground level, lines in blue are the measurements on tower top (HOMs, 35m), or similar heights (trace gas pollutants, 33.6m).
ACKNOWLEDGEMENTS

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REFERENCES


The effect of oxidative aging on chemical composition and volatility of SOA from α-pinene and real plant emissions

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Keywords: α-pinene oxidation, Scots pine emissions, secondary organic aerosol, Potential Aerosol Mass reactor, FIGAERO

INTRODUCTION

Secondary Organic Aerosol (SOA) particles are composed of a large number of compounds with different functionalities, which all contribute to chemical and physical properties, such as viscosity, hygroscopicity and density (Hallquist et. al., 2009). Part of the chemical complexity stems from the large diversity of the initial emissions of volatile organic compounds (VOCs), that are oxidized to form low-vapor pressure products contributing to SOA formation. In addition, the chemical composition of SOA undergoes continuous evolution through reactive uptake of various atmospheric compounds, further oxidation and photochemistry, reactions promoted by aerosol liquid water, etc. These ageing processes and their effects on climate and the effects of SOA on human health remain poorly understood.

The elemental analysis of aerosol particles can be done using on-line aerosol particle mass spectrometry methods, for example with Aerodyne’s Aerosol Mass Spectrometer (AMS) (Aiken et. al., 2008, Jimenez et. al., 2009 and references therein), and molecular composition can be measured with various off-line methods (Pratt et. al., 2012). During recent years, multiple on-line chemical ionization mass spectrometer (CIMS) based methods providing detailed molecular information due to non-fragmenting soft ionization have been developed. Chemical ionization mass spectrometry coupled with thermal desorption methods (such as Thermal Denuder-interface (TD-CIMS, Smith et. al., 2004), Micro Orifice Volatilization Impactor (MOVI-HRTof-CIMS (Yatavelli et. al., 2012.)), Aerosol-ToF-CIMS (Zhao et. al., 2014) and Filter Inlet for Gases and AERosols (FIGAERO-ToF-CIMS (Lopez-Hilfiker et. al., 2014))) has proven to be especially powerful for molecular analysis of particulate organics separated by volatility.

In this study, we used FIGAERO-ToF-CIMS (Aerodyne Research Inc.) to investigate how the chemical composition of polydisperse SOA derived either from α-pinene or from real plant (Scots pine seedlings) emissions changes with increasing level of oxidation. The results show that oxidative aging of SOA particles results in a higher proportion of low-volatility compounds with smaller carbon numbers but higher OS_C ratios. These results are important for understanding the chemical fate of SOA transported over long distances.
METHODS

Secondary organic particles were formed from oxidation of α-pinene or plant emissions using an Aerodyne Potential Aerosol Mass (PAM, Kang et. al., 2007, Lambe et. al., 2011). The chemical composition of the SOA particles was investigated with FIGAERO coupled with chemical ionization time-of-flight mass spectrometer (ToF-CIMS, Aerodyne Inc. and Toferwerk AG) using iodide-adduct ionization (Lee et. al., 2014). In the instrument, the aerosol particles are collected on a Teflon filter and then desorbed into the instrument with gradually heated nitrogen flow, generating temperature-resolved ion signals (thermograms) that are related to the volatility of the collected compounds. SOA size distributions produced by the PAM-reactor were monitored using a Scanning Mobility Particle Sizer (SMPS, TSI Inc.), and average oxidation state of the SOA population was monitored using an Aerodyne Aerosol Mass Spectrometer (AMS). The experimental setup is shown in Figure 1.

![Experimental setup schematics.](image)

The PAM reactor was adjusted to produce three different oxidative conditions and the resulting polydisperse aerosol populations were termed “Low OS_C”, “Medium OS_C” and “High OS_C” corresponding to the average oxidation state of carbon measured by AMS, <OS_C>_{AMS} (table 1). Mass spectrometry data from FIGAERO-ToF-CIMS were analyzed using program tofTools (Junninen et. al. 2010).

RESULTS AND CONCLUSIONS

The temperature integrated mass spectra shown in Figure 2(a) corresponding to the Low OS_C α-pinene oxidation products were similar to previously published results (Lopez-Hilfiker et. al., 2014). However, mass spectra changed significantly as the extent of oxidation increased. For example, the integrated mass spectrum over one heating period from High OS_C ± α-pinene experiment shown in Figure 2(b) is shifted towards lower molecular weight compounds compared to the Low OS_C case.

The thermograms shown in Figure 2(c) of the normalized Total Ion Count (TIC) are also different for each α-pinene experiment (Low, Medium and High OS_C). Both figures include only organic compounds containing C, H and O atoms in the assigned chemical composition. Table 1 lists five assigned compounds with highest signal from α-pinene experiments for each oxidative condition and shows the average oxidative state of carbon measured with FIGAERO-CIMS, <OS_C>_{CIMS} for the whole set of compounds observed in the mass spectra of each experiment. It also show the oxidative state of carbon measured with AMS, <OS_C>_{AMS}. The <OS_C>_{AMS} and <OS_C>_{CIMS} values were calculated based on the approach described in Kroll et. al., 2011. The average oxidation state and peak desorption temperature both increased at higher oxidative conditions while the average molecular size decreased compared to lower oxidative conditions. This is consistent with fragmentation of compounds during photo oxidation observed in
previous experiments with oxidative flow reactors. (Lambe et al., 2011, Bruns et al., 2015, Chhabra et al., 2015).

Figure 2. Panel a) shows integrated mass spectra over one heating period from “Low OS_C”– α-pinene experiment. Red circles label five assigned compounds with the highest signal and their composition. Panel b) shows same information for “High OS_C” – α-pinene experiment and Panel c) shows sample thermograms for each α-pinene experiment.

Table 1. Five assigned compounds with highest signals (in descending order) from each α-pinene experiment. Row below compounds shows the average oxidative state of carbon <OS_C>CIMS for the whole set of compounds detected with FIGAERO-CIMS in each experiment and lowest line shows the same values derived from AMS measurements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Low OS_C</th>
<th>Medium OS_C</th>
<th>High OS_C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{10} H_{16} O_{5}</td>
<td></td>
<td>C_{8} H_{12} O_{5}</td>
<td>C_{8} H_{10} O_{6}</td>
</tr>
<tr>
<td>C_{10} H_{16} O_{6}</td>
<td>C_{10} H_{16} O_{6}</td>
<td>C_{8} H_{12} O_{6}</td>
<td>C_{4} H_{4} O_{6}</td>
</tr>
<tr>
<td>C_{8} H_{12} O_{4}</td>
<td>C_{10} H_{16} O_{6}</td>
<td>C_{7} H_{8} O_{6}</td>
<td></td>
</tr>
<tr>
<td>C_{10} H_{16} O_{4}</td>
<td>C_{9} H_{12} O_{6}</td>
<td>C_{9} H_{12} O_{6}</td>
<td></td>
</tr>
<tr>
<td>C_{8} H_{12} O_{5}</td>
<td>C_{7} H_{10} O_{5}</td>
<td>C_{7} H_{10} O_{5}</td>
<td></td>
</tr>
<tr>
<td>&lt;OS_C&gt;CIMS</td>
<td>-0.25</td>
<td>0.07</td>
<td>0.51</td>
</tr>
<tr>
<td>&lt;OS_C&gt;AMS</td>
<td>-0.45</td>
<td>-0.06</td>
<td>0.62</td>
</tr>
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ACKNOWLEDGEMENTS

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REFERENCES

Jimenez et. al., (2009), Science, 326, 1525-1529.
ZEPPELIN-LED STUDY ON THE ONSET OF NEW PARTICLE FORMATION

H. E. MANINEN1,2, J. LAMPIAHTI1, T. NIEMINEN3, S. MIRME4, M. EHN1, I. PULLINEN5, K. LEINO1, S. SCHOBESBERGER2, J. KANGASLUOMA1, J. KONTKANEN1, E. JÄRVINEN6, R. VÄÄNÄNEN1, T. YLI-JUUTI1, R. KREJCI1, A. MIRME4, S. DECESARI7, G. P. GOBBI8, L. GANZEVALD9, R. TILLMANN3, D. R. WORSnop10,11, F. ROHRER3, T. PETÄJÄ1, V.-M. KERMINEN1, Th. F. MENTEL5 AND M. KULMALA1

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Keywords: Atmospheric aerosols, Boundary layer, New particle formation, Airborne measurements.

INTRODUCTION

We used a Zeppelin as a measurement platform to observe aerosols in the atmospheric layers closest to the ground. Within the PEGASOS project we compared two different type of environments with frequent new particle formation (NPF) observations. In spring 2013 we had the Northern campaign in a clean boreal forest environment at Hytiälä, Finland, whereas in summer 2012 we had the Southern campaign when we measured in more polluted areas at Po Valley, Italy. Our study consists of both airborne and ground-based measurements during both campaigns.

We aim to answer in which atmospheric layer the onset of NPF takes place, and how homogenous the newly-formed particles are within the mixed boundary layer (BL). We observed that the regional NPF events began simultaneously and evolved uniformly inside the mixed rising BL. On vertical scale, we did not observe newly-formed, sub-3 nm particles outside the continental boundary layer (CBL). These newly-formed particles grow inside the full height of the mixed CBL. In addition to the typical horizontal homogeneity of the regional NPF events, on horizontal scale we observed some local component of the NPF bursts.

The majority of the ambient atmospheric measurements are normally done from the ground. Flight measurements are essential to evaluate the representativeness of the ground-based in-situ measurements. Especially when the regional and atmospheric models need emission data and the field observations are used to validate and constrain these models. This project contributed on collecting that kind of experimental data set with in-situ measurements at ground level and airborne measurements in the lower atmosphere.

METHODS

The most important layer of the atmosphere is the lowest two kilometres. That is where we live, where the vegetation is, and where most emissions go. The majority of measurements in that part of the atmosphere are normally done from the ground. We can also use airborne measurements, but the airplanes fly at high
altitudes and their flight speed is very fast. On the other hand, the Zeppelin airship is slow moving – 50 km/h – and we can sample from a stable, agile platform, all levels up to 1000 meters above ground with our aerosol instrumentation. We loaded the Zeppelin with the state-of-art instrumentation, specially designed to collect information on the feedback between the chemical compounds and the smallest aerosol particles to estimate their role to climate and air quality.

These measurements are part of the PEGASOS project which aims to quantify the magnitude of regional to global feedbacks between the atmospheric chemistry and physics, and thus quantify the changing climate. The Zeppelin flights are observing radicals, trace gases, and aerosols inside the lower troposphere over Europe in several locations during 2012-2013. The main nucleation (i.e. particle formation focused) campaigns were performed in the Po Valley, Northern Italy, and Hyytiälä, Southern Finland. The main instruments used to study the onset of NPF in continental boundary layer (CBL) are Particle Size Magnifier (PSM) and Neutral Cluster and Air Ion Spectrometer (NAIS). Aim of this work is to observe the onset of the NPF event.

Comparison between two different environments where NPF is occurring frequently: in suburban area at Po Valley (rural polluted), Italy, and in boreal forest at Hyytiälä (rural background), Finland. In Po Valley total 3 vertical profiles with NPF, and in Hyytiälä only one good profile with NPF event occurring during flight. We performed measurements with an instrumented Zeppelin airship (250-1100 meters a.s.l.) and on a ground-based measurement site both in Po Valley and Hyytiälä. In addition, at Hyytiälä we fly with a CESSNA research aircraft (450-2500 m a.s.l.).

Using Zeppelin, we focused on the time of the rising PBL from sunrise until noon to measure vertical profiles of aerosol particles and chemical compounds. This is the time when NPF typically occurs at ground level. The vertical profile measurements represent the particle and gas concentrations in the lower parts of the atmosphere: the residual layer, the nocturnal boundary layer, and the PBL. At the same time, the ground based measurements records present conditions in the surface layer.

We used a generalized methodology to derive NPF event probability that was used to optimize flying hours during Zeppelin campaign in Finland during the PEGASOS-Zeppelin Northern campaign. Based on the existing knowledge, Nieminen et al. (2015) derived a method for estimating the nucleation probability that utilizes forecast air mass trajectories, weather forecasts and air quality model predictions. With the forecast tool we were able to predict the occurrence of NPF events for the next day with more than 90% success rate (Nieminen et al, 2015).

We aim to answer in which atmospheric layer the onset of NPF takes place, and how homogenous the newly-formed particles are within the mixed boundary layer. On vertical scale, where were the newly formed particles seen? What is the contribution of residual layer and tree troposphere?

CONCLUSIONS

NPF was observed on 4 out of 5 nucleation layout flights during the Po Valley Zeppelin campaign. When particle formation was observed, it was seen both on airborne and ground based measurements. These results show that nucleation and particle growth takes place in the boundary layer not in free troposphere. The high time resolution of the instruments allowed us to observe the starting time, location and altitude of the new particle formation. The results suggest that the new particle formation begins simultaneously inside the mixed and the surface layer but does not take place in the residual layer (Manninen et al., in preparation). A case study from Hyytiälä, measured on May 8, 2013 shows that the regional particle formation begins simultaneously and evolved uniformly inside the mixed layer.

To detect directly the very first steps of new particle formation in the lowest one to two kilometers of the atmosphere, we used airborne Zeppelin and Cessna measurements, and ground based in-situ
measurements. The Zeppelin measurements provided an exceptional data package to study the vertical extension of NPF in the boundary layer. The high time resolution of the instruments on-board allowed us to observe the starting time, location and altitude of the new particle formation events. The onset of NPF was usually observed on-board Zeppelin when it was measuring inside the rising mixed layer which is connected to the surface layer by effective vertical mixing. The newly formed, subsequently growing, nucleation mode particles were observed to be homogeneously distributed inside the mixed layer. The observation of growth and vertical homogeneity suggest that the particles were formed throughout the full height of mixed CBL. This result is limited by the Zeppelin flight altitude but supported by the Cessna flight observations (Väänänen et al. 2016).

The detailed measurements of the mass spectra of the naturally charged ions provide evidence on the composition of these newly formed particles. Sulphur dioxide is an important precursor of aerosol particles. The aerosols affect cloud formation and by doing so they can contribute to the cooling of the atmosphere. By reducing sulphate-aerosols we run the risk of suppressing an effect which actually works against climate warming. We compared two different environments where NPF is occurring frequently: in suburban area at Po Valley (rural polluted), Italy, and in boreal forest at Hyytiälä (rural background), Finland. In the Po Valley, we had total 3 vertical profiles with NPF, and in Hyytiälä, only one good profile with NPF event occurring during flight. In Italy we flew over areas that have a lot of people and a fair amount of industry. We expected to find a fair amount of anthropogenic emissions and high sulphate-aerosols loading. When flying in Finland, we expected observe much more natural biogenic emissions from boreal forest. Therefore, before we can truly understand what humans are doing to contribute to higher aerosol loadings, we also have to really understand the biogenic sources, in addition to the sulphur dioxide loading.

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REFERENCES


ACCURACY OF ‘APPEARENT’ PARTICLE FORMATION RATES CALCULATED FORWARD AND BACKWARD USING THE KERMINEN AND KULMALA EQUATION

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INTRODUCTION

Atmospheric aerosol particles span a range of diameters between less than one nanometer to few hundred micrometers. These particles are the result of primary emissions, such as sea spray, desert dust and combustion particles, or secondary formation in the atmosphere through gas-to-particle formation. After their formation, particles are susceptible to either growth by condensation or loss to available sinks (Kulmala et al., 2013).

In this study we focus here lies on the nanometer-sized particles formed via secondary gas-to-particle transformation. This phenomenon is known as new particle formation (NPF), and it has been observed in many locations around the globe (Kulmala et al., 2004 and 2012). The importance behind NPF rests in its ability to contribute to cloud condensation nuclei (CCN) concentrations, which in turn alter cloud characteristics (Merikanto et al., 2009; Kerminen et al., 2012). Accordingly, NPF may influence climate by changing various cloud properties and is found to result in global cooling (IPCC, 2013).

In order to understand deeply the NPF phenomenon and its accompanying effects, it is important to dig into the properties of particles, starting with their concentrations in different size ranges and formation rates at different diameters. In clean environments, where no major fluctuations in sink or precursor vapor concentrations are observed, Kerminen and Kulmala (2002) derived an analytical formulae to determine the ‘apparent’ formation rate of particles at small sizes based on the observed formation rates from measurements of particles at a larger sizes. Therefore, the formula can be used to estimate the formation rates of particles, which are smaller than those detected with most of the commonly used particle counters. In this work, our aim is to study the accuracy of this method by using long-term data sets in a clean background environment in Southern Finland. With the development of new instruments able to detect particles and ions down to less than 1 nm in diameter, we are able to study the precision of the Kerminen and Kulmala equation for the derivation of ‘apparent’ formation rates.

METHODS

Data for our study were collected from the SMEAR II (Station for Measurement of Ecosystem –Atmosphere Relations, Hari and Kulmala, 2005), from where there is a long term comprehensive data set of particle number size distributions, gas concentrations, meteorological parameters, etc. The SMEAR II station is located in Hyytiälä, southern Finland, and is within a pine forest away from human activities and major anthropogenic pollution. Those features make the station suitable for NPF analysis, as it can be considered a semi-clean background location, which somewhat represents the northern hemisphere boreal forests.

Our analysis was based on the particle number size distributions measured by a twin DMPS (Differential Mobility Particle Sizer) system (Aalto et al., 2001) for the diameter ranges 3-500 nm until 2004 and 3-1000 nm starting from 2005. These data were used for classifying days into NPF event and non-event days using the method by Dal
Maso et al. (2005). The DMPS measurements were also applied for calculating the condensation sink (CS, e.g. following Kulmala et al., 2012) used also in the analysis.

For our analysis, we used the data set covering the period from March 1996 to December 2014. Our focus was on Class I events (Dal Maso et al. 2005), which are NPF events homogenous enough for determining their growth rates. The nucleation mode growth rates (GR) were calculated following the method presented by Hussein et al. (2005), for the Class I events between 1996 and 2014.

While the main aim of our study is to study the accuracy of backward calculation (Using bigger particle sized particles’ ‘real’ formation rates to calculate ‘apparent’ formation rates of smaller ones) using the Kerminen and Kulmala (2002) equation, we are also interested in understanding the accuracy of the forward calculation in order to for example, estimate missing data.

Accordingly, let us assume that we want to do a comparison between the formation rate of 5 nm particles and above (J3) i) determined from measurements (J3,Measured) using DMPS number size distributions and ii) obtained from forward calculation starting from using the J3 measured value of J3 (J3,Calculated). It is important to note that J3 is delayed by a value of GR x (dp2 – dp1).

Measured values of formation rates were obtained according to the formula presented by Kulmala et al. (2012):

\[ J_{dp} = \frac{dN_{dp}}{dt} + CoagS_{dp}.N_{dp} + \frac{GR}{\Delta dp}.N_{dp}, \]  

where the coagulation sink (CoagS) is calculated based on Kulmala et al. (2012) and it describes sink for the formed particles due to their coagulation in larger particles, analogously to CS for vapours.

For example, J3 which is the formation rate of particles in the size range 3 - 25 nm:

\[ J_{3,measured} = \frac{dN_{3-25}}{dt} + CoagS_{3-25}.N_{3-25} + \frac{GR}{\Delta dp}.N_{3-25} \]  

According to Kerminen and Kulmala (2002)

\[ J_{d_{p2}} = J_{d_{p1}} \exp \left( -\gamma \frac{CS'}{GR} \left( \frac{1}{d_{p1}} - \frac{1}{d_{p2}} \right) \right), \]  

where \( d_{p2} > d_{p1} \), and \( CS'(m^2) = CS/4\pi D_1 \), where CS (here determining the CoagS for the particles in size range \( d_{p1} - d_{p2} \)) is the condensation sink and \( D_1 \) is the diffusion coefficient. \( \gamma \) is calculated following the equation provided by Kerminen and Kulmala (2002).

Thus, we calculate formation rate at J5, forward from J3 (calculated using equation (2)) as follows:

\[ J_{5,calculated} = J_{3,measured} \exp \left( -\gamma \frac{CS'}{GR} \left( \frac{1}{3} - \frac{1}{5} \right) \right) \]
RESULTS, DISCUSSION AND CONCLUDING REMARKS

Figure 1. Correlation between $J_{3,\text{Measured}}$ and $J_{3,\text{Calculated}}$ from $J_{3,\text{Measured}}$ (10 min averages from 690 days). The linear regression and correlation coefficient are added to the plot. Results show quite a good correlation.

Our preliminary results show that a good agreement lies between $J_{3,\text{Measured}}$ and $J_{3,\text{Calculated}}$, resulting in a correlation coefficient of $R = 0.81$ (Figure 1). Similar analyses were applied for formation rates at different particle sizes calculated from measurements from different ‘real’ formation rate sizes. For example, $J_7$ was measured and compared to $J_7$ calculated from $J_3$ and $J_5$ individually. Also, measured $J_{10}$ was compared to $J_{10}$ calculated from $J_3$, $J_5$ and $J_7$, and so on. Our results show the good agreement between the measured and calculated values. Based on our analyses of the long term data set, we present the accuracy and precision of the Kerminen and Kulmala equation in different size ranges. Similarly, we will use the same method to compare observed formation rates in sub-3 nm sizes from PSM (Particle Size Magnifier; Vanhanen et al., 2011) and NAIS (Neutral and Air Ion Spectrometer; Manninen et al., 2009; Mirme and Mirme, 2013) to ‘apparent’ formation rates calculated backward using DMPS (3 nm and above) formation rates, and vice versa (forward from PSM sub-3 nm formation rates to ‘apparent’ rates at diameters larger than 3 nm). To form a complete picture, we will present results from multiple instruments in forward and backward pathways. We will apply the same method for different seasons in order to understand the prevailing factors. Our results will determine the applicability of the Kerminen and Kulmala equation in SMEARII station and give indications of its use in other locations. This will be useful for future analyses of data sets for which sub-3 nm measuring instruments are not available and where missing data needs to be estimated.

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REFERENCES


Mirmé, S., and Mirmé, A. (2013): The mathematical principles and design of the NAIS—a spectrometer for the measurement of cluster ion and nanometer aerosol size distributions, Atmospheric Measurement Techniques, 6, 1061-1071.

INTRODUCTION

The aim of this research is to investigate the viability of utilising mobility spectra from IMS coupled to a ApiTOF (atmospheric pressure interface time of flight mass spectrometer) for chemical composition analysis of cluster ions using electrospray-ionisation (ESI) for ambient data from Hyytiälä, Finland, and utilising calibration from known mobility sample chemicals.

In ESI, a small liquid flow is nebulised into an aerosol through a capillary tube that is placed at high potential and provided a stream of an inert gas or air at the needle tip. Ions formed from an analyte molecules may be multiply charged. When entering the drift tube the formed ions encounter hot gas, which assists in the desolvation of the droplets. The solvent evaporates from a charged droplet until it becomes unstable upon reaching its Rayleigh limit. At this point, the droplet deforms as the electrostatic repulsion of like charges, in an ever-decreasing droplet size, becomes more powerful than the surface tension holding the droplet together. At that point the droplet undergoes Coulomb fission, whereby the original droplet 'explodes' creating many smaller, more stable droplets. The new droplets undergo desolvation and subsequently further Coulomb fissions, creating ions of known composition.

ESI is a so-called 'soft ionisation' technique, since there is very little fragmentation. This can be advantageous in the sense that the molecular ion is always observed, however very little structural information can be gained from the simple mass spectrum obtained. This disadvantage can be overcome by coupling ESI with tandem mass spectrometry (ESI-MS/MS), as has been done for this experiment. Another important advantage of ESI is that solution-phase information can be retained into the gas-phase.

IMS is built upon the principle of ion movement in the presence of a stable electrical field. The drift time, $t_d$, is proportional to its electrical mobility, $K$, and dependent on the temperature and pressure of the drift tube.

IMS separates ions in gas phase based on this property $K$, which is sensitive to the shape and mass of the ion as well as ion-chemical interactions with the ambient air or buffer gas. To account for the temperature and pressure dependencies, as well the electrical field, it is common to use $K_0$, the reduced mobility, which is normalised to base pressure and temperature and applied electric field potential $V$.

As IMS is based on electrical mobility and not polarity, it is not limited by solvent or column constraints, as are Liquid Chromatography (LC) or Gas Chromatography (GC). IMS offers species’ separation of isomeric and isobaric compounds that would otherwise be not possible with LC or GC.

This fact has led IMS to be utilised in various applications, such as chemical agent, drug and explosives detection, medical uses as in protein, peptide and amino acid analysis and also Volatile Organic Compounds (VOCs) detection (Eiceman et al. 2013).
The CI-API-TOF instrument consists of three main components: a chemical ionisation inlet (CI), an atmospheric pressure interface (API) and a time-of-flight mass spectrometer (TOF) (Jokinen et al., 2012).

The APiTOF is described extensively in (Junninen et al. 2010). The atmospheric pressure interface (API) guides the sampled ions in atmospheric pressure to a time-of-flight mass spectrometer (TOF). Three chambers, each containing a turbo pump, differentially pressurise the chambers.

IMS separates on the millisecond timescale and thus couples well with time-of-flight (TOF; IMS-TOF) mass spectrometry, which operates on a microsecond timescale (Krechmer et al. 2016). IMS-TOF instruments can acquire multiple mass spectra for each ion mobility spectrum data point (Kanu et al., 2008).

METHODS

An Ion Mobility Spectrometer (IMS) is coupled to a APiTOF with Electrospray-Ionisation (ESI) in the initial stage.

The location from which our data has been collected is the Station for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR II) station located in the boreal forest site in Hyytiälä, Southern Finland (61°51’N, 24°17’E, 181 a.s.l, Hari and Kulmala, 2005).

For the calibration using tetra-alkyl-ammonium halides, (Ude & de la Mora, 2005) and (Viidanoja et al. 2005) provide reference reduced mobilities in air using ESI for many tetra-alkyl-ammonium halides.

A single calibrated theoretical length for the drift region was attempted based on utilising literature reduced mobility values.

The effective length of the drift region is different from the true physical length of the drift tube, due to the electrophysics present in the instrumental setup. Main factors that deviating effective length and true length of the drift tube are electrical field around IMS entrance gate and the time spent by ions in API region of the APiTOF. Therefore, calculating an average effective length of the drift region based on literature reduced mobility values is used as calibration. The calibration compounds include THAB (tetra-heptyl ammonium bromide, m/z=410), TDDAB (tetra-dodecyl ammonium bromide, m/z=691), EMIBF4 (1-ethyl-3-methylimidazolium tetrafluoroborate, m/z=111) and TBAB (tetra-butyl ammonium bromide, m/z=242). The calibration was repeated for different electrical voltage applied, U, and two different temperature values T, 60 degrees Celsius and 80 degrees Celsius.

CONCLUSIONS
Figure 1: Calibration using tetra-alky-ammonium halides. The theoretical length of the drift region was calculated from literature reduced mobility values. Based on the lower temperature data (333K) an average for the length was determined to be 19 cm.

The results of the calibration can be seen in Fig. 1. All monomers and one dimer (THAB, m/z=886) are shown for different electrical voltage U applied, and in most cases for two different temperatures.

At higher temperature, it is possible there is some clustering from water vapour molecules at 80 degrees Celsius, explaining the generally lower effective length of the drift region at that temperature. Apart from the only dimer in the calibration setup (the THAB dimer m/z=886), the length exhibits a minimum for varying electrical field applied, U. The cause of this is still unclear, though length is theoretically related to U by a squared relationship.

The objective of the calibration was to find a single factor to modify, to be as close as possible to the calculated literature reduced mobility values. By simply taking the mean of these theoretical lengths at T=333K, discarding the T=353K values due to possible contamination clustering, we found L=19 cm to calibrate our setup.

In the presentation more details will be shown on ambient measurements with calibrated electrospray ionization ion mobility mass spectrometer.

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REFERENCES
ORGANICS DOMINATING OVER AMMONIA AND SULPHURIC ACID IN FORMATION AND GROWTH OF NEW PARTICLES IN PO VALLEY, ITALY

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Keywords: New particle formation, organics, sulphuric acid, ammonia, mixed layer height.

INTRODUCTION

An intensive atmospheric measurement campaign was conducted at the polluted rural site, San Pietro Capofiume (SPC) station in the Po Valley, Italy from June 9th to July 10th 2012 (the joint Supersito and PEGASOS project). One of the main purposes of this campaign was to characterize the new particle formation (NPF) events and the chemistry of particles during the growth phase. Measurements included aerosol size distributions down to 1.6 nm, properties and composition of particles, concentrations of gases and several meteorological parameters. Sulphuric acid concentration was not measured during the studied period and, therefore, it was calculated with proxy function introduced in Mikkonen et al. (2011a). The proxy was based on measured SO₂ concentration, solar radiation, condensation sink and relative humidity.

Various factors have been shown to affect NPF and subsequent growth in atmospheric conditions in SPC. This study will continue the work of two such papers; Kontkanen et al. (2016), who studied mainly formation and growth of sub 3nm clusters and Mikkonen et al. (2011b) who studied the effect of various meteorological and trace gas variables on the NPF and the growth of newly formed particles to potential CCN sizes. With the extensive set of measurement instruments available in the PEGASOS campaign we will be able to get better characterisation of the physical and chemical properties of new particle formation events.

METHODS

Measured ammonia concentration, sulphuric acid proxy, mixed layer height and other meteorological factors were first set as predictor variables in statistical robust regression model (rlm; Yegorov, 2016) for testing their effect on new particle formation and growth. Concentrations of organic compounds were not measured and thus their effect on particle formation and growth was initially estimated from the residuals of the regression model. Particle formation rate $J_{1.6}$ was calculated in Kontkanen et al. (2016) and growth rate (GR) was calculated with two different methods. Firstly, from the positive ion size distribution introduced in Kontkanen et al. (2016) for size ranges of 1.6-3nm, 3-7nm and 7-20nm, and secondly, based on SMPS data by following the evolution of peak mean diameter of the growing nucleation mode particles (Hamed et al. 2007). Daily averages of the predictor variables for the regression model were calculated within time frame of 8am-4pm for analysing the factors affecting to day-by-day variations of $J_{1.6}$ and GR. This period was chosen since NPF is observed in SPC during these hours (e.g. Hamed et al. 2007).
A monodisperse particle growth model MABNAG (Model for acid-base chemistry in nanoparticle growth; Yli-Juuti et al., 2013) was used to calculate the contribution of ammonia and sulphuric acid to the particle growth and to estimate how large particle mass fraction and gas phase concentrations of organics would be needed to establish the growth seen in the measurements. MABNAG includes representation of condensation and the particle phase acid-base chemistry.

RESULTS AND CONCLUSIONS

The results of the multivariate regression model indicate that sulphuric acid and ammonia could explain roughly half of the variation of $J_{1.6}$ between NPF days. The results from the MABNAG growth model, shown in Figure 1, indicate that organics were the main component in modelled mass fractions. Both of these results highlights the importance of organics in the NPF process. These results are in line with several recent studies, e.g. Tröstl et al. (2016) who have suggested that low-volatility organic vapours contribute significantly to initial growth of newly formed particles.

![Figure 1. Mass fraction as a function of particle diameter predicted with the MABNAG model showing that organics are the main factor driving particle growth.](image)

In addition to daily formation rates, Kontkanen et al (2016) presented diurnal variation of $J_{1.6}$. We also tested the rlm model to $J_{1.6}$ time series within NPF events. For the rapidly fluctuating formation rate the predicting ability of ammonia and sulphuric acid was even lower than for daily rates. This indicates that the current rlm model is not taking account the rapid fluctuations of the measurement series and time lag between $J_{1.6}$ and the predictors. These effects can be taken account with more advanced methods and that is a topic of further investigation.

We also studied the effects of the same predictors in rlm on the growth rate of the newly formed particles. It seems that sulphuric acid has a high contribution to growth rates of smallest particles but the effect of ammonia is low. Notable is that the ammonia concentration in SPC is relatively high as the station is in the most populated area of Italy and in the middle of area with intensive agricultural activities. It is possible that the ammonia concentration is always high enough to contribute the NPF or subsequent growth processes and thus relatively small changes in ammonia concentration detected within the measurement campaign do not cause notable changes in measured $J_{1.5}$ or GR.
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REFERENCES


ATRIBUTION OF AEROSOL LAYERS FROM GROUND BASED LIDAR AND AIRBORNE IN SITU MEASUREMENTS

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Keywords: AEROSOL, AIRBORNE, LIDAR

INTRODUCTION

Atmospheric aerosol are tiny particles in the atmosphere that are not distributed uniformly, and their size and composition vary in time and place. These are some of the reasons why aerosols remain one of the largest sources of uncertainties in the climate predictions (IPCC, 2013). Understanding the vertical distribution of aerosols and their optical properties is important for determining the aerosol direct and indirect radiative forcing (Haywood and Ramaswamy, 1998). Lidar measurements are able to show the evolution of aerosol layers with high resolution in space and time. (Wandinger et al, 2011). More detailed information about particles sizes and concentration but with lower spatial resolution can be obtained by in-situ airborne measurements. Therefore, the main objective of this study was to combine airborne and lidar measurements in order to increase understanding of the development of the aerosol layers in the atmosphere and processes within them.

METHODS AND DATA

A High Spectral Resolution Lidar (HSRL) was deployed in Hyytiälä from March to September 2014 as a part of the US DoE ARM (Atmospheric Radiation Measurement) mobile facility during the BAECC (Biogenic Aerosols – Effects on Cloud and Climate) Campaign. HSRL measures aerosol backscatter and depolarization with 1 second resolution at 532 nm. Airborne campaigns took place in April and September 2014 during the operational time of HSRL. The flight tracks were above Hyytiälä at altitudes below 4 km and at a quite low speed (<200 km/h), which allowed measurements with good temporal and spatial resolution. A Cessna FR172F aircraft was modified to carry instruments including a Scanning Mobility Particle Sizer (SMPS), Optical Particle Sizer (OPS) and a CO2/H2O analyser (LI-COR LI-840). SMPS has a temporal resolution of 10 min and measured particle sizes from 0.1 to 0.23 μm, while OPS has a 10 sec resolution and measuring particle sizes from 0.3 to 9 μm. A schematic measurement set-up can be seen in Fig. 1.

Figure 1. Schematic figure of the measurement setup: high spectral resolution lidar operating continuously in Hyytiälä, with the Cessna airplane, carrying SMPS and OPS, making ascents and descents in the vicinity, within 30 km.
RESULTS

All instruments worked well during a sequence of three days in April from 8th to 10th, thus, this period was chosen for the further analyses. April 9 2014 is one of the case study days. It was a clear sky day with air masses coming from the north and a new particle formation event was detected by ground based measurements at the SMEAR station in Hyytiälä. Two flights were performed by Cessna during this day: from 8 to 10 UTC and from 13 to 14.30 UTC. Figure 2 shows HSRL backscatter cross section from 7 to 10 UTC. Several layers can be seen in Fig. 2: the lowest layer corresponds to a well-mixed boundary layer that reaches from the surface up to 1200 m, then there is a middle layer at 1200-1700 m, followed by an upper layer that stretches from 1800 m to 3000 m. Profiles of LI-COR relative humidity (RH) measurements made on board the aircraft support these layers identification. The highest RH values of 40% is detected at the top of the boundary layer, while a dry layer from 1200 to 1700 m has the lowest values (5-10%). At 1700 m RH starts growing to reach 20% and then stays constant at the upper layer. Radiosonde was launched during the time Cessna was flying and its relative humidity profile is shown in blue on the figure 2. This profile is similar to Cessna and also confirms recognized layers.

![Figure 2. To the right, HSRL backscatter cross section from 7.00 to 10.00 on April 9 2014 measured at the same time as Cessna was flying. To the left, relative humidity profiles averaged for Cessna climb (red) and descend (pink) as well as RH profile from a radiosonde (blue) that was launched at 5.30. The well-mixed boundary layer reaches from surface to 1200 m, followed by a dry layer between 1200 and 1700 m, and finally, a more humid upper layer is situated between 1800 m to 3000 m.](image)

Figure 3 shows aerosol size distributions that were merged together from the measurements of the SMPS and OPS for two flights. The size distributions similar in shape and concentrations were combined into the layers. From three layers in the Figure 3 during both flights the boundary layer had the highest particle concentration in all size ranges. It is interesting to notice that the high concentration of the nucleation mode particles were detected only during the descend of the morning flight. The new particle formation event started while Cessna was flying outside the BL and, thus, small particles were detected only during second part of the flight. During both ascend and descend of the afternoon flight the concentrations of ultrafine particles were already similar and peaked at 20 nm. The middle interface layer was dominated by accumulation mode particles between 0.1 and 0.6 μm during both flights. The lidar usually detects aerosols starting from 0.1 μm, thus stronger scattering is seen for this layer in Figure 2 compared to the upper layer. The upper layer had fewer particles in all size ranges, and no particles smaller than 20 nm were detected during the morning flight. On the other hand, during the afternoon flight some very small particles were observed on several heights of the interface layer and the upper layer. HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model, http://ready.arl.noaa.gov/HYSPLIT.php) backward trajectories were calculated for every 50 m in altitude, and showed that the BL and the upper layer originated from a little bit different locations.
CONCLUSIONS

We observed that the highest concentration of aerosols in all size ranges was found predominantly in the BL. The shape of the size distribution in the upper layer was often similar to the BL but with overall lower concentrations due to dilution of particles into a large volume of air. The interface layer, that connects two neighboring layers, combined properties of both layers. Turbulent mixing ensured lower variability in the size distribution in the BL on short timescales and more variability in the free troposphere. 96-hours back trajectories for every 50 m for the altitudes from 0 to 4 km m.s.l. showed difference in the origin of the air masses. Origin of the air masses, as well as mixing and deposition, affect aerosol size distribution in different layers.

ACKNOWLEDGEMENTS

This work was supported by the Academy of Finland Centre of Excellence program (project no 272041). We also acknowledge the use of HSRL data in collaboration with the U.S. Department of Energy as part of the Atmospheric Radiation Measurement (ARM) Climate Research Facility during BAECC (AMF campaign in Hyytiälä, Finland).

REFERENCES


MARINE ORGANIC AEROSOL SOURCES IN A GLOBAL CHEMISTRY TRANSPORT MODEL

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Keywords: Marine aerosols, sea spray, transport model.

INTRODUCTION

The breaking of ocean waves by wind creates bubbles, which then burst and release aerosols to the air. As presented in the review by Gantt and Meskhidze (2013), the created sea spray aerosol (SSA) contains sea salt and a mixture of organic matter. The ratio of organic matter concentration to sea salt concentration varies according to the surface wind speed and ocean state while the chemical composition of the organic matter is similar to that of the sea water. The organic SSA can act as cloud condensation nuclei and can have a non-negligible impact on climate. In order to estimate the anthropogenic aerosol forcing, the properties of natural aerosols have to be known. Since the organic SSA is a part of the natural background aerosol, its inclusion is important in climate simulations. Further climate impacts can follow if all or a part of the organic content is considered surface active and it can affect the cloud activation properties of marine aerosol (Prisle et al., 2012).

Several different approaches that can be used to include organic SSA in climate models have been proposed. Vignati et al. (2010) used chlorophyll a concentrations as a proxy when calculating the organic fraction of SSA. Their results indicated that marine sources contribute significantly to organic emissions over the oceans. A more detailed approach by Burrows et al. (2014) uses five different categories of marine organic matter to account for physico-chemical processes involved in sea spray formation: proteins, polysaccharides, lipids, humic acid, and geochemically aged and mixed compounds.

The present work considers the inclusion of an organic SSA fraction to the global chemistry transport model TM5 and the assessment of its impact on the global aerosol distribution. Both the organic SSA parametrisation of Vignati et al. (2010) and the more detailed physico-chemical process-based parametrisation by Burrows et al. (2014) were implemented. The monthly mean sea surface concentrations of organic proxies obtained through observations or precursor simulations were used although the longer term plan is to include ones predicted by the PISCES biogeochemical model as a part of the Earth System Model EC-Earth.

MODELLING APPROACH

We studied the organic SSA using TM5 (Huijnen et al., 2010), a global three-dimensional atmospheric chemistry transport model. It has 27 chemical species that are transported according to the meteorological fields from the ECMWF operational forecast data and 15 short-lived chemical
species that are not transported. Emissions in the TM5 come from a variety of anthropogenic, biogenic, and biomass burning sources. Currently, the emissions from the sea spray include only sea salt according to Vignati et al. (2010).

The aerosol processes in TM5 are handled using the coupled M7 aerosol model (Vignati et al., 2004). It represents particles using seven lognormal modes so that four modes are used to describe the soluble particles and three the insoluble particles. The insoluble modes are the Aitken, the accumulation, and the coarse modes while the soluble modes include an additional nucleation mode. Six different aerosol chemical components are considered in the M7: sulfate, black carbon, primary organic carbon, sea salt, and dust.

In order to allow TM5 to be used in studies involving surface active organic SSA, we first extended the TM5 implementation of the approach by Vignati et al. (2010) to contain an organic fraction of SSA emissions. The monthly mean distribution of chlorophyll a concentration was used as the proxy for the organic fraction in the aerosol produced. In a similar manner, the emission parametrisation of Burrows et al. (2014) was implemented using the monthly mean concentrations of proteins, polysaccharides, lipids, humic acid, and geochemically aged and mixed compounds. The applied proxy concentrations were the same as used by Burrows et al. (2014). Following Vignati et al. (2010) M7 implementation, we distributed the emitted SSA from either chlorophyll a or complex organic mixture proxies to the accumulation and the coarse modes as a fraction of the sea salt emissions. Figure 1 illustrates the spatial and intra-annual variability of one of these SSA emission proxies (protein-like organics).

Figure 1: Mean concentration of protein-like mixture on the ocean surface in January (left) and July (right). Blue indicates 0 µMol/l and red indicates 26 µMol/l.

FURTHER PLANS

After the successful implementation of organic SSA emissions into TM5, we proceed toward their inclusion to the Earth System Model EC-Earth. EC-Earth consists of the atmosphere model IFS, the ocean model NEMO with the sea ice model LIM3, the dynamic vegetation-terrestrial ecosystem model LPJ-GUESS, and the TM5 atmospheric chemistry transport model. The different models are coupled using the OASIS coupler. Further details on the version 2 of EC-Earth are given by Hazeleger et al. (2012).

Compared with simulations using an uncoupled transport model, the transition to an Earth System Model is advantageous in several ways. The online solution of the meteorology allows one to resolve the feedbacks between the chemistry and the other components of the earth system. This concerns especially clouds and their formation as cloud physics are not a part of TM5. The inclusion of a dynamic ocean opens up a whole new domain for study and enables interactions between the atmosphere and the ocean to be included in the simulations.

EC-Earth’s ocean model NEMO can be coupled with the biogeochemical model PISCES (Aumont et al., 2015). It simulates the oceanic cycles of carbon, nutrients, and biological productivity using 24
tracers. Four different living compartments (phytoplanktons and zooplanktons) and three different non-living compartments are considered in addition to limiting nutrients for phytoplankton growth, dissolved organic carbon, total alkalinity, and dissolved oxygen. Using marine organic concentrations simulated with PISCES instead of monthly averages allows for a more accurate calculation of organic SSA in the sea spray schemes of Vignati et al. (2010) and Burrows et al. (2014) while providing further opportunities for the study of the effects of marine organic emissions. For example, PISCES coupled with EC-Earth can be used to explore how the ocean circulation responses to warming affect the phytoplankton populations and the resulting impact on the organic SSA fraction.

ACKNOWLEDGEMENTS

The authors acknowledge EU FP7 project BACCHUS (project number 603445) and Nordic Center of Excellence eSTICC. Susannah Burrows acknowledges support from the Department of Energy, Office of Science (BER). This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 717022).

REFERENCES


ARCTIC AEROSOLS AND PARTICLE FORMATION IN NORTHERN GREENLAND

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Keywords: atmospheric aerosols, Arctic research, mass spectrometry.

INTRODUCTION

The Arctic environment is known to be especially sensitive to global warming. Clouds have a key role for the radiative balance in the Arctic environment. Globally, the net radiative effect of clouds is cooling due to their ability to reflect solar radiation back to space. As a contrary of other parts of the world, in the Arctic environment, the clouds often have a warming effect because the longwave radiation gets caught in between the bright ice or snow-covered surfaces and the clouds (Garret et al., 2002) and the solar radiation is scarce during most of the year. Cloud properties and their formation are connected to the aerosol population and their ability to act as cloud condensation nuclei (Dusek, et al. 2006).

New particle formation is a process where molecular clusters form from atmospheric vapours by condensation and later the clusters can grow into larger particle sizes and act as cloud condensation nuclei. New measurement techniques have enabled the study even the first steps of new particle formation. In previous studies sulphuric acid (Sipilä et al., 2010) and oxidized organic compounds (Ehn et al., 2014) have been seen to be responsible of new particle formation. Until recent years the composition of newly formed particles has not been studied in the Arctic. Since there is little if any vegetation in the Polar Regions the organics are not likely to play a significant role in particle formation. Instead there has been observed iodine during new particle formation events (Allan et al., 2015; Sipilä et al. 2016).

The spring time in the Arctic has several interesting features affecting atmospheric chemistry and physics. During the spring, the solar radiation increases fast, in less than two months from total darkness into midnight sun, enabling several air chemistry processes to start. One of these processes is ozone depletion event which has been detected in the Arctic atmosphere after the sun rise (Barrie et al., 1988; Skov et al. 2004, Simpson et al., 2007). During these events the ozone concentration decreases from ~40 ppbv to almost 0 ppbv due to photochemical degradation. These events have been connected mainly to bromine oxides but also to other halogen oxides (Barrie et al., 1988; Simpson et al., 2007, Brooks et al. 2006). Another characteristic phenomenon during the Arctic spring is so called Arctic haze, which means increased particle concentration in the troposphere due to pollution transportation into the Polar Regions (Heidam et al. 2004; Quinn et al., 2007). The otherwise pristine Arctic atmosphere is strongly influenced by anthropogenic emissions and seasonal atmospheric transport and it has clearly higher concentrations of atmospheric aerosols during spring time. In the cold Arctic winter the stratification of the atmospheric surface boundary layer is stable, and the precipitation is low. Due to those reasons the lifetime of aerosols is significantly longer (from 3 to 7 weeks) during the cold time of the year, compared to summer when the lifetime is from 3 to 7 days (Sirois and Barrie, 1999).
We conducted a measurement campaign in the Arctic having three major objectives: 1) to gain more insight into new particle formation and nucleation processes in the Arctic, 2) to characterize Arctic haze and 3) to identify and characterize the changes in atmospheric chemistry from dark to sunlight period.

METHODS

We conducted an intensive measurement campaign called Nordic Center of Excellence “Cryosphere atmospheric Interaction in a Changing Climate (CRAICC)” at the Villum Research Station, Station Nord (VRS) in Northern Greenland (81° 36’N 16° 39’W, Fig. 1). VRS is on a small peninsula Prinsesse Ingeborg Halvø in the vicinity of Station Nord military camp. We used a new, in 2015 deployed, Atmospheric Observatory located about 2 km outside of the military station. The campaign started in mid-February 2015 and continued until the end of August 2015.

Figure 1. The location of Station Nord where also the Villum Research Station is situated

VRS has continuous measurements of meteorological parameters and ozone concentration. Also gaseous elemental mercury, black carbon, filter pack and high volume sampling measurements have been made the last ten years. Particle size distribution of 10 – 900 nm has been measured with Scanning Mobility Particle Sizer (SMPS, Wang and Flagan, 1990) since 2010. During the CRAICC measurement campaign we used several mass spectrometers, particle spectrometers and particle counters in addition to the continuous measurements to study vapour and particle concentrations and the new particle formation on the site.

We had nitrate-CI-API-TOF (Chemical Ionization Atmospheric Pressure interface Time-Of-Flight mass spectrometer, Jokinen et al., 2012) to measure extremely low volatility vapours such as sulphuric acid and molecular clusters. We used acetate-CI-API-TOF (Bertram et al., 2011) to measure low volatility vapours such as formic acid. Ambient ions were measured with API-TOF (Junninen et al., 2010). Particle concentrations of 0.8 – 40 nm particles were measured with Air Ion Spectrometer (AIS, Mirme and Mirme, 2013), sub-3 nm particles were measured with Particle Size Magnifier (PSM, Vanhanen et al., 2010) and the particle composition was measured with an Aerosol Mass Spectrometer (Canagaratna et al., 2007).

CONCLUSIONS
The measurement campaign was successful and we got data from the whole six-month period. We observed several ozone and mercury depletion events between March and May. During ozone depletion events we also observed increased concentrations of chlorine oxides. Generally, the aerosol particle concentrations were low during the measurement campaign, but occasionally we observed elevated particle concentrations and some particle growth events. A measurable concentration of sub-3 nm particle concentrations were observed during these events. The measured vapour concentrations varied between spring and summer time. We detected high concentrations of iodic acid in April – May when the solar radiation was more intense. During the summer time the snow started to melt and the iodic acid concentrations decreased. According to the preliminary analysis, it seems that the composition of particles was different during the spring and summer time. It appears that iodine oxides are important in the spring time particle formation. We observed iodine oxide clusters that are similar that have been seen during particle events in coastal site in Ireland (Sipilä et al., 2016). These results support the results of Allan et al. who detected iodine in Arctic aerosols larger than 30 nm but this is the first time that iodine oxide has been seen in molecular clusters in the Arctic. When the snow started to melt the role of iodine oxides in the particle formation seemed to decrease and the role of sulphuric acid increased. The data analysis is still in progress and we are going to further examine these results.

ACKNOWLEDGEMENTS

We want to thank personnel at the Villum Research Station and Station Nord for their invaluable help during the measurement campaign. We thank the tofTools team for providing tools for mass spectrometry data analysis. The Nordic Center of Excellence “Cryosphere atmospheric Interaction in a Changing Climate (CRAICC)” and Academy of Finland Center of Excellence (272041) are acknowledged for funding the research.

REFERENCES


INTRODUCTION

Recent research has shown that new particle formation (NPF) is an important source of particles in the atmosphere, which influences cloud formation and atmospheric radiative transfer. In the last decades, multiple studies in many different regions analysed the gas-to-particle conversion and the growth of newly formed particles in the atmosphere. Measurements of NPF above the boundary layer have been comparatively rare. The following study investigates the correlation between NPF events on two alpine mountain summits.

METHODS

The data were recorded at the Environmental Research Station Schneefernerhaus at Zugspitze (2650 m AGL) and at Sonnblick Observatorium (3106 m AGL) between 1st of March and 31st of July 2013. Both stations can be characterized by comparable environmental circumstances. The stations are less 150 km linear distance apart and are influenced by the same large scale weather patterns which cause similar local weather phenomena due to comparable landscape and topography. The collected database is a combination of particle size distribution and meteorological data. Particle size distributions (d_p = 10 – 600 nm) were measured every ten minutes with a DMPS (Burkhart et al., 2011, Wonaschütz et al., 2015) at Sonnblick Observatory and an SMPS at Schneefernerhaus, Zugspitze. Daily plots of particle size distributions were categorized into three classes according to Dal Maso et al. (2005). Model data from ECMWF and GFS were used to assess large scale and meso scale weather patterns. Webcam pictures combined with the meteorological parameters such as wind, temperature, relative humidity or solar radiation, and the concentrations of anthropogenic trace gases (like SO_2) were examined at event days and compared to the situation at non-event days to investigate whether NPF is triggered by local meteorology or large scale synoptic weather.

RESULTS

After classification, 21 event days at Zugspitze and 14 event days at Sonnblick were detected. The classification of all 153 days based on Dal Maso et al. (2005) showed following results:
<table>
<thead>
<tr>
<th>Month</th>
<th>Events Sonnblick</th>
<th>Events Zugspitze</th>
</tr>
</thead>
<tbody>
<tr>
<td>March</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>April</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>May</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>June</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>July</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>SUM</td>
<td>14</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 1. Event days at Sonnblick and Zugspitze between 1st of March and 31st of July 2013

The comparison of both research stations showed that the two stations had 13 event days in common. A clear coherence in the timing and growth patterns (Figure 1) can be seen in most of them. The analysis of weather data, model calculations, and webcam images showed that ideal conditions for NPF consist of a certain amount of insolation in combination with vertical exchange through thermally induced slope winds. Events on the mountain tops only took place after contact to the boundary layer.

CONCLUSIONS

Both stations enable a comparison of new particle formation in the region between boundary layer and free troposphere. The results compare well to other studies in the Alps (Herrmann et al., 2015), which show that new particle formation in the free troposphere requires a contact with the boundary layer. The coherence between events on the two stations is confined to similar weather conditions, which cause local thermally driven wind circulations on both stations.

REFERENCES


EFFECTIVE BVOCs EXCHANGE OF BOREAL FORESTS: EMISSIONS VERSUS IN-CANOPY SINKS

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Keywords: BVOC, dry deposition model, boreal canopy, emissions.

INTRODUCTION

A multi-layer BVOCs dry deposition model has been implemented into a 1-dimensional chemical transport model SOSAA (Boy et al., 2011) to investigate the in-canopy sources and sinks of BVOCs. The deposition model for BVOCs was proposed two decades ago (e.g. Wesely, 1989). However, only until recently the detailed single-layer deposition model of BVOCs have been applied to investigate the BVOCs fluxes (Nguyen et al., 2015) and the loss of secondary organic aerosol (SOA) (Hodzic et al., 2014). Therefore the newly implemented multi-layer BVOCs deposition model in this study can provide a new insight on the BVOCs exchange of boreal forest, which is also useful for estimating BVOCs fluxes at the canopy top. The new model can also be applied in large-scale models.

METHODS

The gas dry deposition model was based on the ozone dry deposition model described in Zhou et al. (2017). For BVOCs, the parametrisation method for mesophyll resistance, cuticular resistance, soil resistance and wet skin resistance were extended from Wesely (1989) and Nguyen et al. (2015). The Henry’s law constant values of all species included in current model were obtained from the measurement data if available (Sander, 2015), otherwise they were computed by the software EPI Suite v4.11 with first group method then bond method. The reactivity factors were taken from three values 0 (non-reactive), 0.1 (semi-reactive) and 1 (reactive), which were proposed according to the functional groups of organic compounds (Wesely, 1989; Karl et al., 2010). BVOC emissions were calculated by MEGAN (Guenther et al., 2006) with the standard emission potentials (SEPs) derived from measurement data in previous studies. The SEPs of individual monoterpenes were obtained from their average emission spectra (Bäck et al., 2012).

Several representative compounds were selected to anaanalyse the sources and sinks within the canopy for typical VOCs. Monoterpenes, C5H8, MBO, CH3OH, CH3CHO, CH3COCH3 and HCHO were chosen to verify the model by comparing their modelled and measured fluxes above the canopy. Moreover, these seven compounds along with the sesquiterpenes also constituted the majority of the emitted gases from the ecosystem at SMEAR II. ACETOL was selected as a typical carbonyl compound, together with CH3CHO, CH3COCH3 and HCHO. Four highly oxidised organic compounds, including PINIC oxidized from APINENE, BCSOZOH oxidized from BCARY, ISOP34NO3 and SQbi2` a2bbBQM AA
ISOP34OOH oxidized from C5H8, were selected, because they are extremely low volatile and thus prone to deposit onto surfaces and condensing onto aerosol particles. The compound names used in this study and their common names are shown in Table 1.

The newly implemented model was applied to investigate the BVOCs exchange over a boreal forest canopy at SMEAR II (Station to Measure Ecosystem–Atmosphere Relations II) in Hyytiälä, Finland, in July 2010. The model set-up was the same as that in Zhou et al. (2017) except that the time period of July 2010 was simulated instead of August.

<table>
<thead>
<tr>
<th>Name</th>
<th>Common name</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT</td>
<td>monoterpenes, including α-pinene, β-pinene, Δ3-carene, limonene, cineole and other minor monoterpenes</td>
</tr>
<tr>
<td>SQT</td>
<td>sesquiterpenes, including farnesene, β-carophyllene and other minor sesquiterpenes</td>
</tr>
<tr>
<td>C5H8</td>
<td>isoprene</td>
</tr>
<tr>
<td>MBO</td>
<td>2-methyl-3-buten-2-ol</td>
</tr>
<tr>
<td>CH3CHO</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>CH3OH</td>
<td>methanol</td>
</tr>
<tr>
<td>CH3COCH3</td>
<td>acetone</td>
</tr>
<tr>
<td>HCHO</td>
<td>formaldehyde</td>
</tr>
<tr>
<td>ACETOL</td>
<td>acetal; hydroxyacetone</td>
</tr>
<tr>
<td>PINIC</td>
<td>pinic acid, oxidized from α-pinene</td>
</tr>
<tr>
<td>BCSO2OH</td>
<td>oxidation product of β-caryophyllene</td>
</tr>
<tr>
<td>ISOP34NO3</td>
<td>oxidation product of isoprene</td>
</tr>
<tr>
<td>ISOP34OOH</td>
<td>oxidation product of isoprene</td>
</tr>
</tbody>
</table>

Table 1: Compound names used in this study and their common names.

CONCLUSIONS

The measured and modelled diurnal patterns of fluxes at the canopy top are shown in Fig. 1. The measured fluxes of MT, C5H8+MBO, CH3OH, CH3CHO and CH3COCH3 show a similar diurnal pattern which apparently follows the diurnal patterns of gas emissions. The upward fluxes are approximately zero during nighttime when the emission is low, while they increase after sunrise until about 16:00 in the afternoon reaching the maximum values. For CH3OH and CH3CHO, the deposition also plays a significant role (Fig. 2). Hence, the fluxes can be downward at nighttime (Fig. 1c and 1d). The diurnal variation of fluxes for MT, C5H8+MBO, CH3OH and CH3CHO are well represented by the model results. Although for C5H8+MBO the monthly-averaged daytime flux is underestimated by up to about 0.03 $\mu$g m$^{-2}$ s$^{-1}$ at around 17:00, the values are still in the range of measurement uncertainties. For CH3COCH3, the model underestimates the flux and shows a downward flux in the morning, indicating an overestimation of deposition effect. In contrast, the model shows a larger upward flux than measurement from about 10:00 to 16:00 at daytime, implying missing sources either from emission or chemical production. The monthly-averaged diurnal flux for HCHO is mostly downward and does not show an apparent diurnal pattern. The large uncertainties also indicate that although the deposition may play a significant role in its exchange processes, other effects, e.g. emission and chemical process, can still compete with deposition effect.

The model also provided a possibility to analyse individual sources and sinks within the canopy instead of only net fluxes at the canopy top for different compounds. The relative contributions of emission (Qemis), net chemical production (Qchem), turbulent transport into the canopy (Qturb) and deposition (Qdepo) are shown in Fig. 2. Here Qturb represents the in-canopy concentration...
change of BVOCs due to turbulent transport, which can be positive (downward) as a source term or negative (upward) as a sink term. For those compounds emitted from vegetation, e.g. C5H8 and MT, Qemis is the dominant source. The chemical process is significant for highly reactive compounds, it can act as a net source for isoprene oxidation products ISOP340OH and ISOP34NO3, and as net removal mechanism for SQT. Deposition is the main sink for most compounds except MT, SQT, C5H8 and MBO. The emitted MT, C5H8 and MBO inside the canopy are mainly lost via turbulent transport to the air above the canopy. The bidirectional flux above the canopy for CH3OH result from the competition between emission and deposition.

Figure 1: Measured (points) and modelled (line) monthly-averaged diurnal patterns of fluxes at the canopy top for (a) MT, (b) C5H8+MBO, (c) CH3OH, (d) CH3CHO, (e) CH3COCH3, (f) HCHO. One standard deviation is shown for measurement data with errorbars and modelled data with shaded area.

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REFERENCES


Figure 2: Modelled relative contributions of sources and sinks for different compounds within the canopy.


AEROSOL SIZE DISTRIBUTION AND NEW PARTICLE FORMATION
MEASURED ON A 300 M OBSERVATION TOWER

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²Observation and Forecast Research Division, National Institute of Meteorological Sciences, Jeju, Korea

Keywords: Aerosol, New particle formation, meteorological observation tower, Korean peninsula.

INTRODUCTION

Submicron aerosols have a significant effect on human health, visibility, and climate change. Aerosol can not only absorb or scatter solar radiation but also alter cloud radiative and microphysical properties by acting as cloud condensation nuclei (CCN). New particle formation (NPF) is known to affect submicron aerosol concentration significantly, and eventually the nucleated particles may grow large enough to act as CCN (Wiedensohler et al., 2009). However, not clearly understood are at what altitude NPF actually occurs, what the spatial scale of NPF is, and what the good meteorological conditions are that lead to NPF. To improve our understanding of the effects of aerosols on human health, visibility and climate change, aerosol observation should be carried out in many different places around the world. In this study, we analyze aerosol measurement data obtained from 300 m meteorological observation tower located at a southern coastal rural region of Korea in order to see if we can detect altitude dependence of NPF in this region.

METHODS

A 300 m meteorological observation tower is built at the National Center for Intensive Observation of Severe Weather (NCIO) at a southern coastal rural town of Boseong, Korea (34.76°N, 127.16°E). The meteorological observation tower is equipped with measurement platforms at 11 different altitudes, and the basic meteorological variables are measured at each of the 11 measurement platforms. We carried out intensive aerosol observation at the meteorological observation tower for about two weeks a year for three years. Measurement periods are shown in Table 1. Number concentration of aerosols larger than 3 nm was measured at 300 m and 10 m altitudes by TSI CPC3776 and CPC3025, respectively. Aerosol number size distribution was also measured at the same altitudes by TSI SMPS and DMPS. The aerosol number size distribution ranges measured by SMPS and DMPS were mostly set to be 10-300 nm in mobility diameter and the data were recorded every 3 and 15 minutes, respectively.

<table>
<thead>
<tr>
<th>Year</th>
<th>Measurement period</th>
</tr>
</thead>
</table>

Table 1. Measurement periods in each of the three years.
RESULTS

The average total number concentration of aerosols larger than 3 nm ($N_{CN3}$) measured at the two altitudes are shown in Table 2. There is no significant difference of $N_{CN3}$ between 10 m and 300 m, and it means that aerosols are homogeneously distributed in the planetary boundary layer. The average aerosol number concentrations are about 10,000 cm$^{-3}$ for the three years with no significant difference. So it can be said that the typical value of the aerosol number concentration in autumn in this region is about 10,000 cm$^{-3}$. Figure 1 shows the time variation of aerosol number size distributions at 10 m and 300 m altitudes during the 2016 measurement period. The aerosol number size distributions and total concentrations measured at 10 m and 300 m were very similar, suggesting that the aerosols are homogenously distributed between 10 m and 300 m altitudes. Aerosols of diameters between 50 and 100 nm accounted for the bulk of the total aerosol number concentration and NPF occasionally occurred.

<table>
<thead>
<tr>
<th>Year</th>
<th>10 m (cm$^{-3}$)</th>
<th>300 m (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014</td>
<td>11220±2725</td>
<td>13073±2169</td>
</tr>
<tr>
<td>2015</td>
<td>10073±4301</td>
<td>10410±2989</td>
</tr>
<tr>
<td>2016</td>
<td>12474±12401</td>
<td>10726±8282</td>
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</tbody>
</table>

Table 2. Average and standard deviation of the number concentration of aerosols larger than 3 nm measured at 10 m and 300 m altitudes of the meteorological observation tower at NCIO.

Figure 1. Aerosol number size distribution during the 2016 measurement period at (a) 10 m and (b) 300 m altitudes.

The number of days when aerosol number size distributions were measured at both 10 m and 300 m was 22 days during the entire three year measurement period. NPF events were observed five times during the
22 days. No NPF event was observed only at 10 m or at 300 m altitude during the measurement period. That is, NPF events occurred simultaneously at the two altitudes. Figure 2 shows aerosol number concentrations and size distributions on the NPF event day of 22 October 2016. The aerosol number concentration at 10 m and 300 m altitudes began to increase almost at the same time, and the aerosol number size distributions were also very similar. Aerosol number concentration and size distribution on the other NPF days also showed similar trend. That is, NPF occurred or newly formed particles were transported almost simultaneously within the 300 m altitude range in this region.

![Diagram](image)

Figure 2. Aerosol number size distribution at (a) 10 m and (b) 300 m altitude and (c) total number concentration of aerosols larger than 3 nm on 22 October 2016.

NPF is prone to occur when solar radiation is strong and relative humidity is low (e.g., Boy and Kulmala, 2002; Hamed et al., 2011). In this study, average value of relative humidity was lower and average value of downward short wave flux was higher on NPF days than on non-NPF days, which is consistent with some previous studies mentioned above. Sometimes NPF events occurred under cloudy conditions as Kim et al. (2014) reported NPF events under cloudy and elevated-dust conditions in the Korean peninsula.
SUMMARY AND CONCLUSIONS

Intensive aerosol measurements were made on the 300 m meteorological tower at NCIO established at a southern coastal rural town of the Korean peninsula. NPF events were also simultaneously observed at 300 m and 10 m altitudes and this seems to suggest that aerosols were almost homogeneously distributed within the 300 m altitude range. The favorable conditions for NPF in this region were found to be low relative humidity and strong solar radiation, which is consistent with some previous studies. However, aerosol measurements in this study were limited to autumn season. Because aerosol and NPF characteristics can show significant seasonal variation, intensive aerosol measurements in other seasons are highly required to identify a complete aerosol and NPF characteristics in this region.

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REFERENCES


PARTICLE GROWTH RATES FROM NUCLEATION MODE TO CLOUD CONDENSATION NUCLEI SIZES

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Keywords: PARTICLE GROWTH RATE, AITKEN MODE, ACCUMULATION MODE.

INTRODUCTION

Aerosol particles play a key role in our current lack of understanding of the climate system, and this is largely due to aerosol-cloud interactions (Stocker et al., 2013). In the lower troposphere, particles with diameters \( d_P \) larger than about 50-150 nm are capable of acting as cloud condensation nuclei (CCN; Kerminen et al., 2012). A major, if not dominant, fraction of CCN is suggested to be formed by condensation growth of smaller aerosol particles (Merikanto et al., 2009; Paasonen et al., 2013; Peng et al., 2014; Wang et al., 2017). The origin of these smaller particles may be either atmospheric new particle formation (NPF), anthropogenic combustion or other emissions. The condensable biogenic vapours typically originate from emissions of volatile organic compounds (VOC) from plants (e.g. Hallquist et al., 2009).

The growth rate (GR) of atmospheric particles can be determined for regional-scale atmospheric new particle formation events, during which new particles are simultaneously formed from vapour molecules over a large area (Kulmala et al., 2012). However, the growth of particles after a NPF event can rarely be followed up to CCN sizes, because such an observation would require a huge area of simultaneous NPF and rather homogenous conditions (Kerminen et al., 2012). Since these kinds of observations are encountered only in specific clean environments and even in them only under certain circumstances, the determined GRs cannot be considered as representative for wider-scale analyses. Furthermore, this scarcity of suitable GR data makes it much more difficult to specify the atmospheric vapours contributing to the particle growth up to CCN sizes.

Here, we apply our new automatic method for determining particle growth rates during particle growth episodes, with no need to explicitly follow an observed NPF event. The growth rates are calculated for particles from the nucleation mode to the Aitken and accumulation modes (3 nm < \( d_P < 300 \) nm). We compare the resulting growth rates with the diameter of growing particles and other measured quantities.

METHODS

We developed an automatic method, which searches for roughly monotonic growth periods of particle modes in particle number size distributions measured with a Differential or Scanning Mobility Particle Sizers (DMPS/SMPS). The code considers not only the nucleation mode (\( d_P < 25 \) nm) but also the Aitken (25 nm < \( d_P < 100 \) nm) and accumulation mode (\( d_P > 100 \) nm). The minimum length of a growth period, for which the growth rate (GR) is determined, is 2 hours. An example of a day with several determined growth episodes is depicted in Figure 1. The method was developed and tested using a 21-year-long DMPS data set recorded at the SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005).
Figure 1. An example of the determination of growth rates. White circles show the maxima of the modes fitted to the particle number size distributions, coloured circles indicate the growth episodes and black lines show fits to the maxima during the episodes. Growth rates are obtained as the slopes of these fits.

The determined growth rates are compared with different variables measured at the station, specifically with those that are presumably related to the formation and concentration of condensable vapours, such as the ambient temperature, concentrations of monoterpenes and their oxidants, condensation sink (CS), radiation level, as well as the time of day and diameter at which the growth period was observed.

RESULTS AND DISCUSSION

The particle growth rates (GR) increased with an increasing particle diameter (Fig. 2). However, in the nucleation mode size range the effect of particle diameter on the growth rate was less prominent than in Aitken and accumulation modes, where the growth rate had close to a linear dependence on the particle diameter. This behaviour could be explained by a combination of two different growth mechanisms:

- Thermodynamic condensation of semi-volatile vapours, resulting in a linear relation between diameter growth rate and particle diameter (under constant vapour concentration), seems to dominate in the Aitken and accumulation mode.
- Kinetic (irreversible) condensation of practically non-volatile vapours, associated with no diameter dependence of the growth rate, seems to be important in nucleation mode.

In agreement with our results, Yli-Juutti et al. (2011) reported that the GRs of nucleation mode particles (3-20 nm) increased with particle diameter especially during the summer.

Figure 2. Determined growth rates as a function of the initial diameter of the growth episodes (see Fig. 1). The colour bar indicates the mean temperature during the growth event.
We inspected the dependence of the particle growth rate on temperature in 10 nm size bins. In all size bins with diameters below 90 nm, the growth rate increased exponentially with increasing temperature. The correlations were significant ($p < 0.001$), but the temperature still explained only a small fraction of the variation in GR for each size bin (the highest correlation coefficient was $R = 0.31$). On the contrary, for the size bins with diameters above 120 nm, the growth rate decreased with an increasing temperature, but the weak correlations were significant only for the size bins between 130 and 170 nm.

The positive correlation between temperature and GR, and its form of an exponential function, suggest that this dependence is caused by the temperature dependence of VOC emissions from the vegetation. This is supported by the corresponding correlations between GR and monoterpane proxy concentrations from Kontkanen et al. (2016) in the similar size ranges. Also Yli-Juuti et al. (2011) reported similar dependences of GR on temperature and monoterpane concentration for the $d_p < 20$ nm size range. However, the explanation for the negative correlation in larger sizes is unclear: even though the volatility of the vapours decreases with temperature, thus enhancing condensation, this effect would be expected to affect also the GR of particles at smaller sizes.

As the next steps, we will inspect whether the variation of GR in size bins could also be associated with some other variables than the temperature and monoterpane concentration.

CONCLUSIONS

We have generated an automatic method to determine aerosol particle growth rates in nucleation, Aitken and accumulation modes. This method increases drastically the number of analysable particle growth episodes, since it allows, in our understanding, for the first time the determination of particle growth rates for time periods not immediately following a new particle formation event.

Our results show that the growth of particles in Aitken and accumulation modes has close to a linear dependence on the diameter of the growing particles. This suggests that the main mechanism causing the growth is thermodynamic condensation of semi-volatile vapours following the Raoult’s law. For the particles in nucleation mode, the kinetic (irreversible) condensation of extremely low-volatile vapours seems to have a significant effect on the growth rates, since the effect of particle diameter on the growth rate is less pronounced. The simultaneous involvement of these two condensation mechanisms is in agreement with results by Riipinen et al. (2011), who studied how well the modelled condensation mechanisms replicate the observed evolution of particle number size distributions.

For particles in the nucleation and Aitken mode, the growth rate was observed to correlate positively with the ambient temperature, whereas in the accumulation mode an anti-correlation between these quantities was observed.

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REFERENCES


10 YEARS OF CLOUD DROPLET ACTIVATION DATA FROM PALLAS ATMOSPHERE-ECOSYSTEM SUPERSITE IN SUB-ARCTIC FINLAND

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Keywords: aerosol-cloud interactions, DMPS, long time series.

INTRODUCTION

The interactions between aerosol particles and clouds cause the largest uncertainty in our estimate of present day radiative forcing compared to pre-industrial time (IPCC, 2013). The most important question is cloud formation, specifically which particles activate into cloud droplets and which do not (McFiggans et al., 2006). This has been studied a lot in simulation chambers and in ambient air during measurement campaigns (eg. Sun et al., 2006). Continuous measurements with cloud condensing nuclei (ccn) counters have allowed us to investigate the particles’ ccn-potential, i.e. which ambient particles would activate in a given supersaturation of water in the air (eg. Burkart et al., 2011). This approach, however, does not tell which particles really do activate in the formation process in a real cloud, as the supersaturation can vary significantly as function of time and location even within a single cloud.

An indirect method to investigate the number and size distribution of activated particles is to measure the particles inside a cloud simultaneously via two inlets, one allowing the cloud droplets to enter the measurements and one blocking them. Once water is evaporated from both particle populations, they are comparable and the difference between them refers to those particles that have been activated into cloud droplets (Komppula et al., 2005).

Conducting this type of measurements at a mountain or hill top site (being frequently within cloud) allows long time series of ambient cloud droplet activation data. This enables investigation of seasonal and inter-annual variation and trends in climate-relevant time scales. We have measured particle number size distribution (PNSD) with this method at Sammallunturi measurements site (24.12°, 67.97° N, 565 m asl), located at a hill top at Pallas Atmosphere-Ecosystem Supersite (Lohila et al., 2015) in Finnish Lapland for more than a decade. Our visibility data started at 1995, PNSD data without cloud droplets in 2000 and with cloud droplets in 2005. All these measurement series are ongoing and continuous except for short gaps.

METHODS

There are two parallel Differential Mobility Particle Sizers (DMPS) at the site, measuring the number concentration and dry size distribution of atmospheric aerosol particles. One DMPS is connected to gas line inlet, which prevents particles larger than about 5 μm from entering the sample line. The other DMPS is connected to a total air inlet with a much larger, yet undefined, cut-off diameter. After each inlet the particles are dried to evaporate any water in them. Subtracting the gas-line PNSD from the total air-line PNSD gives the PNSD of those particles that have activated into cloud droplets. Aerosol particles with very small diameter are not expected to activate into cloud droplets but can be scavenged by the larger droplets or evaporated during the evaporation of water in the particles (Komppula et al., 2005). Therefore only particles with diameter ($D_p$) larger than 50 nm are included in this analysis. We performed the data analysis for hourly-averaged data. Periods when visibility or particle number-size-distribution were changing significantly during the hour were excluded from the analysis.
The measurement site is located on a hill top, about 300 m above the surrounding lowlands. The presence of a cloud at the measurement site was based on visibility, and defined as horizontal visibility < 900 m. This is roughly in line with the synoptic definition of fog (AMS, 2013), and is also supported by particle activation measurements. Activated fraction of particles (Act%) was close to zero during higher visibility, but increased sharply when visibility was below 900 m (Figure 1).

![Figure 1. Mean activated fraction of three particle diameter ranges as function of visibility.](image)

The presence of cloud at the top of Sammaltunturi was also estimated from Ceilometer measurements of cloud height at Kentärova, a low land site at 6 km distance from the Sammaltunturi site. Sammaltunturi site was assumed to be inside cloud whenever the cloud height at Kentärova was less than the altitude difference between the sites.

RESULTS

The site was found to be inside cloud (in-cloud time, $T_{cloud}$) for 23 % of time during the entire time span of the measurements. Annual mean $T_{cloud}$ varied from year to year, ranging from 15 % in 2003 to 29 % in 2012 (Figure 2). Both methods of estimating $T_{cloud}$ give similar numbers and similar interannual variability, with high and low values of $T_{cloud}$ occurring at same years. When only the time periods with cloud but no precipitation were included, this variability pattern remained.

![Figure 2. Annual fraction of time for which the measurement site was inside cloud, and annual mean particle number concentration.](image)
There was also a clear seasonal pattern in $T_{\text{cloud}}$, the measurement site being inside cloud most often ($T_{\text{cloud}} = 46\%$) in November and least often ($T_{\text{cloud}} = 9\%$) in June (Figure 3). This pattern was similar for all the measured years, and remained when precipitating clouds were removed. A more detailed analysis of the Ceilometer data also revealed that the main difference between the summer and autumn clouds was the cloud height, not the temporal coverage of clouds. In winter months there were also cases with very thin low clouds, leaving the Sammallunturi site above the cloud.

![Figure 3. Mean monthly patterns of time for which the measurement site was inside cloud and particle number concentration.](image)

Aerosol particle number concentration, $N_p$, (for particles with diameter between 50 nm and 500 nm) showed a similar inter-annual pattern at the site when compared to $T_{\text{cloud}}$ (Figure 2). No significant correlation between these parameters at annual level were found. The seasonal patterns of $T_{\text{cloud}}$ and $N_p$ were, however, very different (Figure 3). Where $T_{\text{cloud}}$ peaks strongly in autumn, $N_p$ peaks in summer. This also means that even though the low clouds at the site are most frequent in fall, the more rare low summer clouds have highest number of potential ccc. The high particle number concentration in summer clouds leads to increase of $D_{50}$ activation diameter (diameter at which 50% of particles with that diameter activate), which is shown in Figure 4. Also the optically thickest clouds (in-cloud periods with lowest visibility) were observed in summer.

![Figure 4. Mean monthly pattern of $D_{50}$ activation diameter during times when the measurement site was inside cloud.](image)
CONCLUSIONS

This research demonstrates that visibility can be used as a proxy for the measurement site being inside a cloud, and that 1000 m visibility is a good separation criterion between in-cloud and outside-cloud periods. We observed signs of similar inter-annual patterns in cloudiness and particle number concentration. The seasonal patterns, however, were very different from each other. Even though highest in-cloud time fractions were observed in the fall months, the highest number concentrations of activated particles and highest D50 activation diameters were observed in summer.

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REFERENCES

HYGROSCOPIC CONTRIBUTION OF SEMI-VOLATILE SPECIES TO CCN-RELEVANT AEROSOL

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Keywords: aerosol, hygroscopicity, composition, volatility

INTRODUCTION

Atmospheric aerosols significantly influence the climate through their direct interaction with radiation and cloud forming capacity. Both roles are affected by their hygroscopicity, or capacity to adsorb water vapor. In part, this property is governed by the chemical composition of the aerosol and extensive studies have been performed to constrain the compositional influence on hygroscopicity. These have met with mixed success due to the complex and dynamic mixtures of compounds present in most atmospheric aerosol. Further research is particularly required for semi-volatile organic aerosol species as these are the most dynamic components and undergo extensive changes through aging processes in the atmosphere (Seinfeld and Pankow, 2003).

Numerous studies have examined the hygroscopic contribution of these semi-volatile components (e.g. Hong et al., 2014, Johnson et al., 2004, Sellegrin et al., 2008). Where compositional measurements have been available, typically these correspond to the bulk aerosol sample and require the chemical characteristics of the semi-volatile component to be inferred. These approaches have led to inconsistent results, with limited agreement regarding the hygroscopic contribution of different aerosol species (Villani et al., 2013). In part, this can be attributed to the great range of chemical species present in atmospheric aerosols and the challenges associated with uniquely classifying them.

Donahue et al. (2012) has proposed the use of a two-dimensional volatility basis set which characterizes aerosol components by their relative volatility and average carbon oxidation state (OSc). In response to this, recent studies by Cerully et al. (2015) and Hildebrandt Ruiz et al. (2015) examined hygroscopic and compositional changes after removing semi-volatile aerosol fractions. In both cases, the hygroscopic measurements were performed with a cloud condensation particle counter (CCNc). The hygroscopic and compositional characteristics of multiple components were successfully separated. Despite this, there were no apparent trends linking these properties. This highlights the need for further investigation using alternate techniques and aerosol sources.

METHODS

An alternative real-time sampling technique has been developed in this study, using a volatility and hygroscopicity tandem differential mobility analyzer (VH-TDMA) and a compact time of flight aerosol mass spectrometer (AMS). The use of a VH-TDMA, rather than a CCNc, makes this system particularly suited to field measurements of atmospheric aerosol since it reveals hygroscopic differences in externally mixed aerosol samples. The VH-TDMA takes a size-selected aerosol sample and optionally heats it in a thermodenuder. The resulting size distribution is then remeasured with a scanning mobility particle sizer (SMPS), revealing any size reduction due to desorbed semi-volatile species. A second size distribution is also obtained after passing the sample through a humidifying region, allowing calculation of the hygroscopic growth factor (HGF) for heated or unheated aerosol.
In this study, each SMPS consists of a custom-built differential mobility analyzer (DMA) and a TSI 3010 condensation particle counter. The thermodenuder is a compact model with no cooling section, a maximum temperature of 450 °C and a residence time of approximately 2 s. Relative humidities (RH) between 20-90% can be set in the humidifier and the initial size-selecting DMA can select particles between 20 – 250 nm. These sampling parameters can be varied throughout the experiment to obtain volatility profiles, reveal deliquescence and efflorescence characteristics, or investigate size-dependent variations. Doing this reduces the time resolution of the observations and often is not suited for variable aerosol sources, as is observed in atmospheric sampling. For this reason, most measurements in this study were performed with a thermodenuder temperature of 120 °C, humidifier RH at 90%, and three or fewer pre-selected particle sizes.

The AMS provides aerosol non-refractory chemical composition with unit mass resolution and other authors have discussed its operation in detail (e.g. Drewnick et al., 2005). As shown in Figure 1, the AMS has been integrated into the VH-TDMA with a series of computer-triggered valves which allow the thermodenuder to be cycled between each instrument. Comparison between the composition of heated and unheated aerosol allows chemical characterization of the semi-volatile component and correlation with its contribution to particle hygroscopicity. Since size-resolved compositional analysis can be inconclusive for low concentrations or variable sampling conditions, AMS measurements are usually based on ensemble averages for aerosol between 50 - 600nm.

![Figure 1. Schematic of the integrated sampling system allowing the AMS and VH-TDMA to alternately sample heated and unheated aerosol. The blue and dotted green arrows represent the alternate flow paths.](image)

The VH-TDMA size distributions are inverted using the TDMAinv procedure (Gysel et al., 2009), to adjust for non-idealities in the DMAs and separate distinct particle size modes within externally mixed samples. From the resulting HGPs, particle hygroscopicity is modelled with composition-dependent $\kappa$ values, using the $\kappa$-Köhler method (Petters and Kreidenweis, 2007). The relative hygroscopicity of the semi-volatile component can then be separated, as per the Zdanovskii, Stokes & Robinson empirical mixing rule (Chen et al., 1973). By correlating variations in this hygroscopic contribution against chemical changes in the semi-volatile component, its associated emission sources and atmospheric processing pathways are investigated.

The AMS uses electron ionization which causes extensive molecular fragmentation and prevents direct chemical identification. However, the semi-volatile component is characterized by examining common marker fragments, determining the OSe value, or by identifying distinct contributing factors through
positive matrix factorization (Paatero and Tapper, 1994). Where a volatility profile has also been obtained, this can be paired with the OS_e value to classify the component under the 2D-VBS.

CONCLUSIONS

As a proof of concept, this sampling system was used to study ammonium sulfate-seeded secondary organic aerosol (SOA), generated through photolytic oxidation of α-pinene in the presence of ozone. Over a period of 3 hours, the SOA was formed in an 8 m³ teflon chamber, illuminated by UV lights. Alternating heated and unheated measurements were performed throughout this time, with the thermodenuder set to 120 °C and the RH at 90%. To maximize time resolution, only 100 nm particles were examined with the VH-TDMA. Figure 2 demonstrates both the long-term increase in organic concentration as the SOA formed, and the regular changes in organic and sulfate concentrations and hygroscopic growth factor (HGF) as the sample was alternately cycled between the thermodenuder and the bypass lines. Prior to significant SOA formation, there was limited volatility and little change in HGF. As the less hygroscopic SOA fraction condensed, this more volatile fraction created larger HGF variations until it dominated the particle phase and could not be entirely desorbed in the thermodenuder.

![Figure 2. Alternating heated (triangles) and unheated (circles) measurements of aerosol hygroscopic and chemical properties for α-pinene + O₃ SOA formation on ammonium sulfate seed particles. Compositional measurements have been shifted by -3 minutes to bring them into sync with the HGF measurements.](image)

The sampling system has been deployed to several Australian field measurement campaigns, targeted at significant regional sources of climate-relevant aerosol. These include measurements of biomass-burning emissions from savannah fires in the Northern Territory, baseline marine aerosol from the northwestern coast of Tasmania and coastal emissions near the Great Barrier Reef. Results from these campaigns will be presented, demonstrating the source-dependent differences in the hygroscopicity of semi-volatile components.

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REFERENCES


CONTRAILS IN A WEATHER FORECAST MODEL - INFLUENCE ON CIRRUS CLOUDS AND THE RADIATION BUDGET

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Keywords: contrails, cirrus, aircraft emissions, radiation, NWP

INTRODUCTION

Contrails consist of ice crystals formed in the exhaust plume of aircraft due to the entrainment of environmental air. They only occur alongside the special environmental conditions described by the Schmidt-Appleman-Criterion (Schumann, 1996). With a favorable state of the atmosphere, characterized by temperatures below around -40 °C and supersaturation with respect to ice, the originally line-shaped contrails undergo various physical processes at the micro scale, spread by the influence of shear and advection and change their structure and microphysical properties until they are no longer distinguishable from natural cirrus. This type of anthropogenic cloud is called contrail cirrus (Heymsfield et al., 2010). Under very favorable conditions, they survive for several hours.

Important properties, such as the optical depth or the spatial and temporal extent of occurrence, have not been sufficiently investigated and are also not quantified to a satisfactory extent (Boucher et al., 2013). One class of model studies uses global circulation models extended by parameterizations that are able to simulate contrails (Burkhardt and Kärcher, 2011). The major drawbacks with applying these methods are the coarse resolution of the models both in space and time. Another class of studies approaches single contrails with large-eddy models (Lewellen et al., 2014; Unterstrasser, 2014). For young contrails, the evolution of ice crystals in the exhaust plume and the fluid dynamics of wake vortex formation and decay are represented in detail. Subsequently, the contrail-to-cirrus transition involves a complex interaction of shear- and sedimentation-driven dispersion, depositional growth and radiative effects. Parameter studies allow for investigating the conditions under which contrails are persistent and the manner in which microphysical and optical properties change during transition and decay. Because this method is not applicable for a larger number of contrails, it is not suitable to quantify the impact of air traffic on the state of the atmosphere. The spatial scale applied in this study lies between those typically used for large-eddy simulations and global climate models. In this respect, the presented study is complementary to the aforementioned approaches and is, to our knowledge, the first study of its kind. The online coupled regional numerical weather forecast and chemistry model system COSMO-ART (Baldauf et al., 2011; Vogel et al., 2009) is extended by a parameterization based on recent results of large-eddy simulations (Unterstrasser, 2016) for taking the formation of contrails into account. In this context, online coupled means that meteorology, chemistry and contrail-related processes are simulated in one model at the same grid and using one main time step for integration.

Ice crystals in young contrails are considerably smaller than the ones that form in natural cirrus clouds and occur with a substantially higher ice crystal number density (Febvre et al., 2009; Voigt et al., 2010). Therefore, the original microphysical scheme was extended by new hydrometeor classes that allow for a separate treatment of the small ice crystals in contrails and contrail cirrus apart from natural ice. Besides, a fractional coverage for contrails (Bock and Burkhardt, 2016) is implemented to consider the sub grid scale character of young contrails depending on the model resolution. This approach allows for the investigation...
of contrail microphysical properties and their changes during the various stages of development represented in a regional atmospheric model.

Regarding the contrail microphysics and the interaction with the meteorological situation, the entire procedure is online coupled, thus allowing feedback processes between contrails and natural clouds in contrast to other models on a comparable grid scale (Schumann, 2012). One of the key goals of this study is thus to quantify the influence of contrails and contrail cirrus on natural high-level cloudiness.

In addition to the contrail microphysics, the radiative properties of contrails and contrail cirrus and their local influence on the shortwave radiative fluxes at the surface are also examined.

The model uses a diagnostic radiation scheme (Ritter and Geleyn, 1992). The description of the optical properties for contrail ice is adopted from the description of the optical properties for naturally occurring cloud ice crystal habits (Fu et al., 1998).

Hence, the presented model configuration serves to study microphysical evolution of contrails and contrail cirrus; their influence on natural high-level cloudiness; and their impact on the radiative fluxes on a regional scale and short time periods. This gains importance, e.g., in predicting the energy yield from photovoltaic systems, as additional cloud cover due to contrails is not represented in operational weather forecasting.

Another feature of this study is the new and recently developed data set of real time flight tracks. Rather than statistical calculations for globally averaged fuel consumption, the basic data consist of real time-based flight trajectories (flightradar24.com, 2016).

MODEL DESCRIPTION

In the following, a short overview of the parameterizations used to calculate the microphysical properties of ice crystals and the modifications to represent contrails are presented.

In this study, the COSMO-ART model is coupled with a comprehensive two moment microphysical scheme following Seifert and Beheng (2006). Until now, the scheme contained besides classes for cloud droplets, rain, graupel and hail, only one class of ice crystals that occur in high-level ice clouds optimized for ice crystals in natural cirrus. Because ice crystals in freshly formed contrails are considerably smaller than those in natural cirrus, the basic microphysical processes in young contrails and contrail cirrus are treated in separate, newly introduced classes. Consequently, also in the radiation scheme, contrails and contrail cirrus are treated separately from the natural cloud ice using the new classes. Similar approaches using climate models with coarser grid size are described by Burkhardt and Kärcher (2009) and Bock and Burkhardt (2016).

Besides a separate class for contrail cirrus, several age classes are introduced for contrail ice. This method allows a better representation of the evolution of mean ice crystal radii and number concentrations that change rapidly in young contrails. Besides, each contrail ice class is characterized by a mean contrail volume. The contrail volume develops similar to a passive tracer in the wake of an aircraft depending on time and wind shear following Dürbeck and Gerz (1996).

In case that the age of a class exceeds a certain threshold or given that the volume of the class is in the order of the grid cell volume, the corresponding contrail ice is transformed to the contrail cirrus class. The different classes of cloud ice, contrails, and contrail cirrus are allowed to interact with each other. This procedure allows the life cycle of young contrails and their influence on natural cirrus to be studied and avoids a diagnostic treatment of the relevant processes. Hence, contrails, contrail cirrus, and natural high-level clouds can compete for the available water vapor.

In the cloud microphysical scheme, the geometrical and microphysical properties of hydrometeors are characterized by various coefficients that describe shape, sedimentation velocity, or ventilation (Seifert and Beheng, 2006). For ice crystals in contrails and contrail cirrus, the same shape for ice crystals is assumed like used for the natural ice. Consequently, the ice crystals in contrail cirrus and contrails are assumed to be hexagonal columns (Seifert and Beheng, 2006).

The descending movement of the primary wake of an aircraft causes adiabatic heating within the plume. Due to this, sublimation and loss of ice crystals occurs, even in a supersaturated environment (Unterstrasser, 2016). As the spatial and temporal resolution of the model is too coarse to simulate these
processes, a parameterization is used to calculate the initial ice mass and number of contrail ice crystals, described in detail in Unterstrasser (2016). Compared to global modeling studies, this study uses a new and recently derived data set of flight motions. Rather than statistical calculations for globally averaged fuel consumption, the basic data consist of exact flight trajectories over a limited area that are recorded from real time-based data (flightradar24.com, 2016). In addition to time, height and geographical position of the aircraft, information on aircraft type, current velocity, fuel consumption, and emission of water vapor is also available. For the actual simulations, the flight trajectories and the corresponding aircraft information are read online at each model time step.

The atmospheric radiative fluxes in the COSMO-ART model are calculated using the GRAALS (General Radiative Algorithm Adapted to Linear-type Solutions) radiation scheme (Ritter and Geleyn, 1992). For the contrail cirrus and contrail ice crystals, the radiative properties are computed using a parameterization following Fu et al. (1998).

RESULTS

Several case studies are performed to investigate how microphysical properties such as ice water content, ice crystal number density and the mean crystal radius of ice crystals in contrails and contrail cirrus change over time and depend on the meteorological conditions. The ice water content in young contrails is comparable to that in thin cirrus clouds ranging from 0.2 to 5.0 mg m\(^{-3}\), but with considerably higher ice crystal number densities between 20 cm\(^{-3}\) and 50 cm\(^{-3}\) and ice crystal mean radii below 20 µm. In the later stage of contrail cirrus, the ice water content grows, the mean ice crystal diameter grows to an extent comparable to that of natural cirrus but ice crystal number concentrations are still higher than in natural cirrus.

Because the cloud microphysics scheme is online coupled to the model, the feedback mechanism between contrails and the surrounding cirrus and the total amount of available water vapor could be quantified. Comparison with satellite data shows good agreement and proves advantages of considering contrails and contrail cirrus in a regional weather forecast model.

Contrail cirrus tend to replace natural cirrus to a remarkable extent and cause changes in the microphysical appearance of high-level cloud coverage, which in turn influences the radiative effect in these regions.

In addition, the impact of contrails on shortwave and longwave radiation can be quantified. The values of the simulated extinction coefficients of contrails and contrail cirrus range from 0.02 km\(^{-1}\) to 2.0 km\(^{-1}\), in accordance with previous in situ measurements and large eddy simulations.

For a case in December 2013, when solar zenith angles are low and the length of days is short, a strong influence of contrails and contrail cirrus is still simulated. They inhibit up to 10 % of shortwave radiation from reaching the ground at noon.

This study is the first approach to simulate contrails and contrail cirrus using a numerical weather prediction model with high spatial and temporal resolution. Subsequently, the presented method can serve as a basis for improving the predictability of the solar radiation in regional weather forecasting by taking into account contrails and contrail cirrus.
REFERENCES


EXTRACTING PARTICLE SOLUBILITY THROUGH COMPARISONS OF CCN AND PARTICLE SIZE DISTRIBUTIONS

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Keywords: CCN, CLOUD PROCESSING, SOLUBILITY, PARICLE SIZE DISTRIBUTIONS.

INTRODUCTION

Aqueous oxidation, collision and coalescence, and Brownian capture by cloud droplets are processes that modify atmospheric particles known as cloud condensation nuclei (CCN). These processes add material to the activated CCN and increase CCN size upon evaporation. Cloud processing thus converts Aitken mode (unprocessed) particles to accumulation mode (processed) particles. Particle size distributions from Differential Mobility Analyzers (DMA) have frequently observed these two modes near clouds (i.e. Hoppel et al., 1985, 1986; Van Dingenen et al., 1995, Clarke et al., 1996, 2013; Tomlinson et al., 2007; Kliemman et al., 2012; Noble et al., 2017). CCN distributions from the DRI CCN spectrometers have also observed both modes (Hudson et al., 2015). Apart from particle size changes, aerosol-cloud processing can change particle solubility ($\kappa$; Petters and Kreidenweis, 2007). Aqueous oxidation of trace gases adds soluble material changing $\kappa$. Collision and coalescence combines two activated CCN. If $\kappa$ is different between them then $\kappa$ changes, otherwise it remains the same. Similarly, Brownian capture combines activated CCN with smaller unactivated particles. If $\kappa$ is different between them then $\kappa$ changes, if not, $\kappa$ is unchanged. Understanding changes in $\kappa$, can provide valuable insight into aerosol-cloud processing.

METHODS

Measurements for this study are taken from two field campaigns: MArine Stratus/Stratocumulus Experiment (MASE), and Ice in Cloud Experiment-Tropical. DMA particle size distributions and CCN distributions were measured in both aircraft campaigns. A measure of bimodality of these distributions can be determined by distribution shape and the relative concentrations in each mode. The amount of bimodality is quantified on a 1-8 scale where 1 is the most bimodal and 8 is strictly unimodal. Modes that have varying degrees of shoulders or tails are the intermediate values. This modal rating (distribution shape) is related to cloud droplet number concentration and mean diameter (Hudson et al., 2015; Hudson et al., 2017). Bulk chemistry measurements were also made during MASE, simultaneous to the CCN and DMA measurements. The various chemical species were sorted and averaged according to the 1-8 modality scale of the corresponding distributions.

DMA particle size distributions can be compared to CCN distributions in order to determine $\kappa$. CCN distributions are plotted using critical supersaturation ($S_c$). However, DMA distributions are plotted by particle size. A $\kappa$ assumption converts the DMA distributions to $S_c$. Therefore, various $\kappa$ are applied to DMA distributions to best match the CCN distributions (Fig. 1). Figure 1 displays CCN-DMA distribution comparisons using the corresponding best $\kappa$ value. At times, the CCN spectrometer had higher concentrations than the DMA (Figs. 1A, low $S_c$ processed mode, and 1D, unimodal), as the DMA may miss larger particles during the size stepping needed to measure the full distribution. While at other times, the DMA had higher concentrations than the CCN spectrometer (Figs. 1A and 1C, unprocessed modes at high $S_c$) because the CCN spectrometer does not measure smaller less soluble particles. Figure
1B shows a good comparison for both instruments. For bimodal distributions, each mode (processed and unprocessed) may be matched. Sometimes, the same κ provided the best fit for each mode (Figs. 1A and 1C). However, many times different κ provided better individual fits for each mode (Fig. 1B).

![Graphs showing comparisons of particle distributions from DMA (colors) and CCN (black) measurements. DMA size is converted to S_c by assuming solubility (κ). Examples from ICE-T.](image)

**RESULTS AND CONCLUSIONS**

MASE bulk chemistry measurements pointing to chemistry changes with increasing bimodality. Greater amounts of sulfate (Fig. 2A, black) and nitrate (Fig. 2B, green) were related to corresponding bimodal CCN distributions (low modal rating). Unimodal distributions (higher modal rating) had lower sulfate and nitrate. Likewise, bimodal distributions were associated with less sulfur dioxide (Fig. 2A, red) and ozone (Fig. 2B, blue), suggesting uptake and removal of these gases by cloud droplets through aqueous oxidation within the droplets.

![Graphs showing MASE chemistry measurements by modal rating. a) Sulfate and sulfur dioxide; b) nitrate and ozone.](image)
Table 1. κ mean and standard deviations (mn; sd) for processed (κp), unprocessed (κυ) and unimodal conditions (κ’un). Also for κυ compared with κp. # is the number of data and % is the percent of the total number of data (MASE=135; ICE-T=76).

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<tr>
<td>κυ&lt;κp</td>
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<td>0.25</td>
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<tr>
<td>κυ&gt;κp</td>
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Mean κ from DMA-CCN comparisons for each field campaign are shown in Table 1. Overall, κ was higher in MASE than in ICE-T; and mean κ of the processed mode (accumulation; κp) was higher than mean κ of the unprocessed mode (Aitken; κυ) for both campaigns. ICE-T had more bimodality (91%) overall because 41% of MASE distributions were unimodal. ICE-T also had higher frequencies of κυ and κp equal (43% to 25% in MASE). This suggests dominance of physical processing in ICE-T where combining CCN of the same composition does not change κ. Larger updrafts in the cumulus of ICE-T compared to the MASE stratus support this finding (Hudson et al., 2015). The greater increase from κυ to κp in MASE than ICE-T (0.45 to 0.50 vs. 0.38 to 0.39) suggests dominance of chemical processing in MASE where aqueous oxidation adds soluble material. This larger difference is mostly influenced by the 29 MASE cases where κp is greater than κυ (0.73 to 0.60); while the 17 cases where κp is less than κυ are not very different (0.40 to 0.44). However, in ICE-T the difference is larger when κυ is greater than κp (0.30) but has less influence on the mean difference between κυ and κp than the difference when κυ is less than κp (0.20) due to fewer cases (13 vs. 23).

As stated previously, chemical processing adds soluble material which alters κp from κυ. In MASE, 58% of bimodal spectra show κ differences while in ICE-T 52% show κ differences (Table 1). Figure 3 also shows that chemical processing dominates in MASE while ICE-T is largely dominated by physical processing. In MASE when κυ was high (>0.75), κp was lower (Fig. 3A). And when κυ was lower (0.3-
The increase in sulfates and nitrates for bimodal distributions (Fig. 2) suggest that the addition of these soluble materials from chemical cloud processing increase low κₐ (e.g., organics adding sulfate) and decrease high κₐ (e.g., sea salt adding sulfate) as seen in Figure 3A. Figure 3B shows something similar for ICE-T at high κₐ but with other κₐ the relationship to κₚ is less clear. It can be argued that at the lowest κₐ in ICE-T, κₚ increases (Fig. 3B) suggesting some chemical processing. However, the large majority of the data suggests little difference between κₐ to κₚ which supports physical cloud processing (likely collision and coalescence) in ICE-T.

Polluted MASE stratus were dominated by chemical processing while ICE-T cumulus were dominated by physical processing (Hudson et al., 2015), however, both types of processing were found in both field campaigns. Comparing CCN distributions with DMA particle size distributions provides a new method for obtaining particle solubility (κ). This determination of κ is simple and straightforward once the data are collected. Determining κ provides information about cloud processing type which agreed with previous data analysis.

ACKNOWLEDGEMENTS

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REFERENCES


ESTABLISHING THE IMPACT OF MODEL SURFACTANTS ON CLOUD CONDENSATION NUCLEI ACTIVITY OF SEA SPRAY AEROSOLS

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Keywords: AEROSOLS, CLOUD CONDENSATION NUCLEI, HYGROSCOPICITY.

INTRODUCTION

Aerosol impacts on cloud properties, also known as indirect effects, remain a major source of uncertainty in modeling global radiative forcing. Reducing this uncertainty necessitates better understanding of how aerosol chemical composition impacts the cloud-forming ability of aerosols. The presence of surfactants in aerosols can decrease the surface tension of activating droplets relative to water and lead to more efficient activation. The importance of this effect has been debated, but recent surface tension measurements of microscopic droplets indicate that surface tension is substantially depressed relative to water for lab-generated particles consisting of salt and a single organic species (Ruehl and Wilson, 2014) and for complex mixtures of organic matter (Ruehl et al., 2012). However, little work has been done on understanding how chemical complexity (i.e., interaction between different surfactant species) impacts surface tension for particles containing mixtures of surfactants. In this work, we quantified the surface tension of lab-generated aerosols containing surfactants that are commonly found in nascent sea spray aerosol (SSA) at humidities close to activation using a continuous flow stream-wise thermal gradient chamber (CFSTGC). Surface tension was quantified for particles containing single surfactant species and mixtures of these surfactants to investigate the role of chemical complexity on surface tension and molecular packing at the air-water interface. For all surfactants tested in this study, substantial surface tension depression (20-40 mN/m) relative to water was observed for particles containing large fractions of organic matter. Mixing surfactants together impacted kinetic limitations to particle water uptake.

METHODS

Lab-generated SSA proxies consisted of known amounts of NaCl and marine-relevant surfactants, including myristic acid (C14 saturated fatty acid), palmitic acid (C16 saturated fatty acid), and oleic acid (C18 unsaturated fatty acid) (Cochran et al., 2015). Particles were humidified in a CFSTGC, where the equilibrium size of the humidified particles was quantified. Relative humidities (RH) ranging from 99.3 to 100.6% could be achieved by varying the temperature gradient of the instrument. Particles containing multiple surfactants were also collected for offline gas chromatography analysis to quantify the relative fractions of each surfactant species. The combination of the dry particle size, wet particle size, and RH were used to calculate surface tension using the compressed film model (Ruehl et al., 2016), which accounts for partitioning of surfactants between the surface and bulk of the droplet. In this model, surface tension is only depressed relative to pure water once a full monolayer is formed. Further addition of surfactants leads to rapid surface tension depression up to some minimum value. Surfactants added
beyond this minimum value partition into the bulk droplet, i.e. dissolve, leading to a plateau in the surface tension when the organic-to-salt ratio is very large. The observations demonstrate that substantial surface tension depressions are observed for mixed salt-organic droplets near the point of activation.

CONCLUSIONS

It was observed that for mixed salt-surfactant particles at RH ~99.9% the extent of surface tension depression exhibits an inverse relationship with the molecular area available to surfactants at the air-water interface, which is determined by a combination of RH and organic volume fraction. The onset of surface tension depression occurs at a composition-dependent critical molecular area; this critical molecular area corresponds to the formation of a full monolayer. Surface pressure-molecular area isotherms indicate that the extent of surface tension depression for microscopic droplets can be larger than that observed for bulk solutions. The critical molecular area was dependent on the specific surfactant tested, indicating differences in molecular packing at the air-water interface. Surface pressure isotherms of two-component surfactant systems (e.g. oleic acid + myristic acid) shared properties of the individual components, such as critical molecular area or minimum surface tension. For some systems, however, surface pressures could not be predicted via a simple molar-weighted average. Kinetic limitations were observed for particles coated with just palmitic acid, since palmitic acid molecules inhibit water uptake through their ability to pack tightly at the surface. However, these kinetic limitations disappeared when palmitic acid was mixed with oleic acid, indicating a disruption in packing. Substantial decreases in surface tension of particles containing marine-relevant surfactants suggest that the impact of surface tension may be important in the activation of nascent SSA. Previous studies (Collins et al., 2016; Ovadnevaite et al., 2011) have observed higher than expected CCN efficiency for SSA particles, given the very large organic content of SSA < 200 nm. A reduction in the droplet surface tension near the point of activation could explain this discrepancy. Efforts to determine whether the surface tension depression observed for the systems investigated in this work at RH values very near 100% persists as droplets continue to grow up to their critical supersaturation are ongoing.

Figure 1. (A) Measured wet droplet diameter for 200 nm NaCl particles coated with variable amounts of oleic acid at 99.9% relative humidity as a function of dry coated particle diameter. The red line corresponds to the predicted droplet growth assuming surface tension = 72 mN/m. (B) Surface pressure derived from the compressed film model as a function of molecular area for NaCl particles coated with oleic acid. Full monolayer coverage occurs at molecular areas < 50 Å².
ACKNOWLEDGEMENTS

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REFERENCES


THE IMPACT OF AEROSOL COMPOSITION ON MICROPHYSICAL CLOUD PROPERTIES OBSERVED AT MACE HEAD, IRELAND

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Keywords: ground-based remote sensing, microphysical cloud properties, optical cloud properties, stratiform liquid water clouds, air mass transport.

INTRODUCTION

Aerosol-cloud interactions contribute largely to uncertainties in quantifying the Earth’s radiation budget. We combined profiling of cloud properties with aerosol concentrations near the surface to address this problem. Ground-based remote sensing observations of microphysical cloud properties have been done at the coastal site of Mace Head, Ireland, since 2009. Mace Head is situated at a unique location at the West coast of Ireland, enabling the observation of air masses transported over long distances, advected over the Atlantic, as well as local pollution and the outflow of anthropogenic pollution from the European continent (Jennings et al., 2003).

METHODS

The ground-based remote sensing division at Mace Head consists, among others, of a 35 GHz Ka-band Doppler cloud radar (Bauer-Pfundstein and Goersdorf, 2007), a CHM15K ceilometer from Luft (former Jenoptik) (Heese et al., 2010; Martucci et al., 2010) measuring at 1064 nm, and an RPG-HATPRO water vapour and oxygen multi-channel microwave profiler (Löhnert et al., 2009; Martucci and O’Dowd, 2011).

Homogeneous single-layer non-precipitating water clouds were selected from a data base of more than six years. A total of 118 cloud cases were classified as marine (23 cases), marine modified (55 cases), continental (26 cases) and continental modified (14 cases) according to three-day back trajectories from the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory (Draxler and Rolph, 2014). This data set and the microphysical cloud properties were discussed by (Preißler et al., 2016). The microphysical cloud properties effective radius ($r_{\text{eff}}$), cloud droplet number concentration (CDNC) and liquid water content (LWC), as well as cloud albedo and cloud optical thickness (COT), were retrieved from combined measurements of cloud radar, ceilometer and microwave radiometer using the retrieval algorithm SYRSOC (SYnergistic Remote Sensing Of Clouds)(Martucci and O’Dowd, 2011).

In this study, ground-based in-situ aerosol characteristics were investigated for those 118 cloud cases. Included were mass concentrations of black carbon, detected by a multiangle absorption photometer; sulphate ($\text{SO}_4$), organic matter, sea salt and nitrate ($\text{NO}_3$) detected by an aerosol mass spectrometer (Ovadnevaite et al., 2014); and volume concentration of cloud condensation nuclei (CCN). We also investigated chlorophyll-A concentrations observed by MODIS (Moderate-Resolution Imaging Spectroradiometer, on Aqua satellite) in the North Atlantic, west of Mace Head.
RESULTS

Figure 1 shows correlation plots of effective radius and $SO_4$ concentration. Plotted are data sets containing all clouds (top), and clouds observed during day-time only (bottom). Considering the data set of all cloud cases, the shown correlation is poor. Ground-based in-situ aerosol measurements are only representative of aerosol load near cloud base in well-mixed conditions. Therefore the case selection was restricted to cloud cases observed between 9:00 and 17:00 local time. The bottom plots in figure 1 show an improvement of the correlation coefficient between $SO_4$ concentration and effective radius. However, due to the reduction of data points the significance decreased (increased p value).

Analysis of the other ground-based in-situ aerosol concentrations showed that some aerosol compounds, namely $SO_4$ and organics, correlate better with CDNC than others, like sea salt. We found positive correlations of CDNC from remote sensing with $SO_4$ and organics. Consistently, cloud droplet effective radius is negatively correlated to $SO_4$ and organics. CDNC also correlated with chlorophyll-A concentrations, which is a proxy of biological productivity in the Ocean. Larger chlorophyll-A concentrations would suggest higher emissions of primary marine organics and thus an increase in CDNC, which is reflected in CDNC correlation with chlorophyll-A concentrations.
Cloud optical depth and cloud albedo are positively correlated to SO$_4$, CCN and organics. Generally, CDNC, COT and cloud albedo were lowest in air masses arriving at Mace Head from the ocean, and highest in continental air. Correspondingly, effective radius was largest in marine air masses.

CONCLUSIONS

An improvement of correlations between the remotely sensed microphysical cloud properties and ground-based in-situ aerosol concentration by narrowing down the cloud cases to daytime observations was expected and could be confirmed. We will further improve the representativeness of the results by considering only clouds which are coupled to the boundary layer. At the conference we will present relationships between cloud properties ($r_{\text{eff}}$, CDNC, IWC, cloud albedo, COT) and aerosol concentrations measured in-situ near the surface (BC, SO$_4$, organic matter, sea salt, NO$_3$) as well as near-surface CCN and satellite observed chlorophyll-A.

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REFERENCES


CLOUD PARTICLES DISTRIBUTION IN A THUNDERSCLOUD

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Keywords: THUNDERSTORMS, NUMERICAL SIMULATION, CLOUD PARTICLES, ATMOSPHERIC ELECTRICITY.

INTRODUCTION

Well-known that there is a close relationship between electrical and microphysical processes between cloud particles: electric field formation and charge separation interconnect to dynamics of air flow, moisture distribution and phase composition of the cloud. It is especially important for the thunderclouds since lightning discharges are the greatest threat to human, technical devices and engineering structures. For this moment the atmospheric electric field is insufficiently studied due to the lack of in-situ measurements in cumulus clouds at the mature stage. However, there are possibilities to use output data of numerical weather prediction models for explicit algorithms of thunderstorm forecast and analysis of spatio-temporal microphysical and electrical characteristics. Such techniques are based on computation of the electric field.

The aim of presented work is the explicit electrification and lightning forecast using Cumulonimbus (Cb) electrification model implemented within the WRF-ARW (Weather Research and Forecast) model. WRF-ARW model has an option of many cloud microphysics parametrizations. In current research Thompson, Purdue Lin and WDM6 schemes including vapor and 5 classes of hydrometeors (ice and snow crystals, graupels, rain and cloud droplets) are studied (Lim, 2010; Lin et al, 1983; Thompson et al, 2004). So the objectives of this study are:

1. Physical and mathematical description of the Cb electrification model.
3. Sensitivity test results of thresholds of the electrical characteristics of solid particles in Cb for the lightning activity occurrence to the type of used WRF-ARW microphysics parameterization schemes.

METHODS

The possibility of using the electrification model for the thunderstorm forecast is studied in this research. Cb electrification model uses output obtained from hydrodynamic mesoscale model WRF-ARW: profiles of hydrometeors’ fractions (snow, ice particles and graupels), cloud water content, air temperature and vertical wind component in the layer of 1020-300 hPa.

Cb electrification model is a set of equations describing the processes of charge generation and separation in convective clouds, constants and profiles of meteorological data. Charge generation process is described by equations taking into account the diameters of interacting hydrometeors (snow, ice particles, graupels, cloud droplets), their concentration, the fraction of particles between which there was a collision /merger, the resulting charge from a collision/merger, gravitational speed of particles’ sedimentation and air temperature (Gardiner et al, 1985; MacGorman et al., 2001; Mansel et al, 2005; Ziegler et al., 1991). The model includes the equations describing non-inductive, inductive mechanisms and its combination - the integrated schemes of charge generation.

Non-inductive mechanism of the charge generation implies the interaction of solid hydrometeors (ice crystals+graupels, particles of snow+graupels). Inductive charging equation implies the interaction of
graulpels and cloud droplets (Zeigler et al., 1991). Pairwise interaction between other hydrometeors is neglected because of the small charge generated as a result of the collision/merger between particles (Latham and Mason, 1962; Gaskell, 1989; Mansel et al., 2005).

Charge separation unit of the electrization model includes equations of the total volume charge, potential and electric field intensity.

CONCLUSIONS

Maximum concentration and terminal speeds of solid hydrometeors and their total space densities strongly depend on used WRF-ARW microphysics parameterization scheme. So there are no any common thresholds for the lighting prediction. Model spatio-temporal microphysical and electrical characteristics do not contradict the results obtained experimentally in studies of electricity in thunderclouds and radar maps of observed convective cells (Mansell, 2005).

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REFERENCES


AEROSOL PHYSICO-CHEMICAL AND CCN PROPERTIES IN AND AROUND ANTARCTICA DURING THE AUSTRAL SUMMER

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Keywords: Cloud condensation nuclei, maritime polar and continental Antarctic air mass, physico-chemical properties

INTRODUCTION

The marine environment is an important source of aerosol primary [C. D. O’Dowd and Leeuw, 2007; G. de Leeuw et al., 2011; Vignati et al., 2010] and secondary production [Myriokefalitakis et al., 2010; Rinaldi et al., 2010]. In marine environments isolated from anthropogenic activity, natural biological components can alter the chemical and physical composition of those aerosols [O’Dowd et al., 2015]. In the Antarctic Ocean, algal blooms occur in the open ocean but also under permanent and temporary sea ice in the Weddell Sea [Arrigo, 2014]. The temporary ice, will often break and separate during the summer season, although remain unmanageable for ships to navigate. Cold water algae will have high quantities of DMSP [Simó, 2001] (Usually more DMSP found in biological blooms in colder water [Gabric et al., 2005] which is precursor to MSA, a chemical component associated with new particle formation (NPF) [Charlson et al., 1987; Dawson et al., 2012; Leaitch et al., 2013] leading many to believe that these regions may have inject large contributions of organically rich sea spray into regional aerosol.

Organic enrichment has been seen to increase CCN activation efficiency of marine particulates, even those that are already efficient CCN [Ovadnevaite et al., 2011]. Findings like this has led to the expectation of increased CCN in areas of biological enrichment, such as algal blooms in otherwise “clean” (black carbon < 2 ng/m³) or anthropogenically unaffected areas. Earth system models (ESM) use biological enrichment parametrisations of CCN activation to better resolve cloud formation over the marine environment. To do this they need a way to track biological activity with good correlation to biological enrichment. Tracking biological enrichment has, therefore, been a hot topic. There is evidence to suggest that satellite retrievals of chlorophyll-a (chl-a) density in marine waters might be the best available way to mark areas where organic enrichment can be expected [O’Dowd et al., 2015; Rinaldi et al., 2013]. Algal blooms, once thriving, enrich sea-spray with organic matter as the bloom enters its demise phase and in fact a time lag of this chl-a retrieval and organic enrichment has been shown [O’Dowd et al., 2015; Rinaldi et al., 2013]. However, it has also been suggested that a persisting carbon pool on the marine surface layer is responsible for organic carbon enrichment, without influence from local biological events. This would suggest chl-a as a poor source for tracking biological enrichment [Quinn et al., 2014], but is in stark contrast with the results of O’Dowd et al., [2015].

Previous studies [Davison et al., 1996] have shown polar air masses arriving from the Antarctic continent to the South Atlantic and Antarctic Oceans were shown to consist primarily of H₂SO₄ in the accumulation mode size range, with inferred NH₄⁺ to SO₄²⁻ molar ratios close to zero. By comparison, air masses of temperate maritime origin were significantly neutralized with molar ratios of ≫ 1. Events of new particle formation were identified in the Weddell Sea and occurred under conditions of high DMS flux and low aerosol surface area.
This region is particularly of interest due to its minimal influence of anthropogenic inputs and probably is the most pristine and biologically-rich, region of the planet. Equally so, the impacts of anthropogenic influence can be clearly quantified and the aerosol-cloud system is also quite susceptible to perturbations, making it a unique natural laboratory to study this system.

The primary objective of this study is to characterise aerosol properties as a function of air mass history, or origin.

METHODS

The PEGASO cruise, on board the Research Vessel Hesperides, took place as a joint National University of Ireland Galway – Barcelona Marine Institute of Science effort to elucidate climatological processes through the investigation of biological, physical, and chemical components of the Antarctic marine waters. The Hesperides, departed from Barcelona in September, 2015, and arrived in the Southern Ocean in December, 2015, after which it traversed the Southern Ocean in the Austral summer (January – February, 2015). The ship path can be seen in red in figure 1. An extensive suite of aerosol instrumentation for a combination of in-situ ambient measurements, sea water extraction, and bubble-tank experiments were employed during the cruise. The study reports on the physico-chemical properties of marine and (Antarctic) continental aerosol encountered in the region over January and February, 2015.

Multiple instruments were employed for in-situ ambient measurements during the campaign. Meteorological activity was monitored and recorded throughout the cruise. There was then sampling off of laminar flow lines to an HR-Tof-AMS, a TSI standard SMPS, a TSI standard CPC (range 10nm -3um), and the continuous-flow streamwise thermal-gradient CCN counter (CCNC) commercially available from Droplet Measurement Technologies, Inc.[Roberts and Nenes, 2005; Rose et al., 2008]. The CCNC was set-up using a DMA system to size segregate the aerosol samples [Paramonov et al., 2013; Rose et al., 2010]. Eleven sizes were scanned, each for 60 s, with mobility diameters ranged from 20-244 nm against five supersaturations ranging from 0.08 -1.48%. The first and second size scan were both 20 nm to allow CCNC temperatures to stabilize. Critical diameters could then be extracted at a minimum time resolution of one hour. Critical diameters were later used in conjunction with the SMPS to find the average hourly total CCN at varying supersaturations. Origin of arriving aerosols were resolved from 120 hr back trajectories from HYSPLIT [Stein et al., 2015], using a starting point of 100 m AGL on ship’s GPS position.

RESULTS AND CONCLUSIONS

Air masses are large bodies of air that have been influenced by large scale homogeneous surfaces (land or sea). They generally reach characteristic temperatures and humidities after sustained influence of surface fluxes over many days. Their meteorological properties are typically invariant within the air mass and the air masses are also associated with synoptic scale meteorological systems. Notable changes in the meteorological parameters are normally only associated with frontal passage, representing a change in air mass. Similar to pseudo-steady-state meteorological parameters being characteristics of air mass origin,
atmospheric composition parameters (e.g. reactive gases and aerosols) are also expected to possess pseudo-steady-state characteristics. In classifying air masses, we filter the dataset for extended periods of relatively stable or invariant meteorological and atmospheric composition characteristics, setting stability over 4 hours as the minimum requirement for selection and inclusion into the air mass characterisation database.

Four main air mass influences were observed; three maritime polar, (mP), air masses, and one continental Antarctic (cAA) air mass. The first mP comes from the region of the Southern Ocean, West of Argentina, the second from the region East of Argentina, and the third is a modified mP influenced by the Weddell Sea. The cAA air is also modified due to Weddell Sea influence. One example of each is presented in Figure 1.

Weddell Sea modification seems to play a heavy role in the aerosol chemistry of observed cases, with a heavy emphasis on non-sea-salt-SO$_4$ (nss-SO$_4$), domination. Activation efficiency for CCN follows a slope indicative of nss-SO$_4$, with low levels of sea salt contributing to increase activation efficiency at larger sizes. The lack of sea salt contributions can be seen in a lower mass-volumetric mode event in the larger particle sizes. The mP air masses are distinct in that, in many of the cases, particle number in the Aitken mode was almost doubled to that associated with the accumulation mode. However, due to the larger fractional contribution of sea salt, the mass-volumetric contribution increases at larger diameters.

The results also indicated that while organic mass fraction, nss-SO$_4$, NH$_4$, and organic nitrogen can be correlated to CCN numbers, chlorophyll-a (chl-a) mass satellite retrievals do not correlate to CCN number. However, there is a strong correlation between enriched organic fraction [O’Dowd et al., 2015] and chl-a.
Figure 1. Aerosol chemical and physical characterization, broken down by case. Each case has 4 columns, A, B, C, and D. [A] Air mass back trajectories extracted from HYSSPLIT [Ralph, 2016; Stein et al., 2015]. In red, PEGASO cruise ship path. In blue, 120 hr back trajectory ending 100m AGL directly above location of ship. On trajectories, (A) denotes the trajectory from start of the case period, (B) denoting the middle, and (C) the end. The larger the letter the greater the air mass height (0-1000m above sea level). [B] Particle number (black) and volume (blue) size distributions. On left, number distribution, with case variability shown in grey. On top are the total average number of particles cm$^{-3}$ (N), and total average particulate volume cm$^{-3}$ (V). [C] Pie chart of chemical mass fractions in cases. On top, total mass m$^{-3}$ is listed, followed by black carbon mass m$^{-3}$ (BC). [D] CCN activation efficiency slopes. Graph shows critical supersaturation against critical diameter, case slope shown in black, and expected/accepted values of ammonium sulphate shown in red and sodium chloride shown in green from AP3 model [Rose et al., 2008].

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REFERENCES


Rolph, G. D. (2016), Real-time Environmental Applications and Display System (READY) Website edited, NOAA Air Resource Laboratory, College Park, MD.


Simó, R. (2001), Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links., *TRENDS in Ecology & Evolution,* 16(6).


INTERACTION BETWEEN AEROSOL AND LIQUID CLOUDS IN BORELA FOREST ZONE

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Keywords: AEROSOL-CLOUD INTERACTIONS, BIOGENIC AEROSOLS, BOREAL FOREST.

INTRODUCTION

Aerosol-cloud interactions (ACI) stay in focus of many research groups due to the high complexity of involved processes and lack of collocated long-term measurements of aerosols and clouds. Meteorological drivers and state of boundary layer affect cloud formation and life and, therefore, pose significant difficulties in attributing changes of observed cloud properties to the modification in aerosol loading. Biogenic Aerosols – Effects on Clouds and Climate (BAECC) campaign (Petäjä et al, 2016) that took place at the SMEAR II station in Hytjälä, Finland, made possible collection of data that can be utilized to study ACI in boreal forest domain. It combined set of active remote sensing instruments such as lidars and radars with comprehensive aerosol measurements. It is expected that concentration of biogenic secondary organic aerosol (BSOA) formed in the boreal forest environment will increase due to the growing temperatures and enhanced emission of precursor vapors by plants. BSOA can grow to the cloud condensation nuclei (CCN) sizes and participate in cloud processes, particularly in low-level warm clouds. Our study gives insight into the ACI in the active BSOA formation zone.

METHODS

We used methodology presented in Sarna and Russchenberg (2016) to retrieve cloud effective radius (Re) that allows investigating indirect effect of aerosols on clouds. Warm low-level clouds occurred during five months (April–early September) throughout campaign time and are the subject of this study. We combine measurements from W-band ARM Cloud Radar (WACR), microwave radiometer and CCN counter together with Cloudnet target classification dataset. Among parameters used in this study are surface CCN concentration, liquid water path (LWP), cloud phase and cloud depth (CD). Rigorous data filtering had to be applied to ensure appropriate selection of profiles. Single layer liquid clouds with cloud base height not greater than 2000 m were considered. All profiles that have LWP smaller than 5 g m⁻² and profiles with detected ice were discarded. Re is retrieved for non-precipitating profiles only from radar reflectivity and LWP assuming gamma cloud droplet distribution is constant with height in each of the profiles. Re at 80 meters above detected cloud base is used to draw conclusions on ACI.

RESULTS AND CONCLUSIONS

Theory predicts increase of Re with increase of LWP in cloud column and with cloud depth. Data collected during BAECC campaign fully follows this prediction as shown on the Figure 1a. Re grows with LWP and CD and reaches values up to 5.5 µm at cloud depths above 450 m and LWP greater than 120 g m⁻². Re also showed connection to the surface CCN levels (Figure 1b). For a constant LWP level, lower cloud effective radius relates to the greater CCN concentrations measured at the surface. Numerous studies showed that at SMEAR II station located in Hytjälä aerosol population is dominated by BSOA, therefore we can attribute with high level of confidence observed changes in the clouds’ microphysical properties to the biogenic aerosols concentration.
Figure 1. (a) Retrieved Re for low-level liquid non-precipitating clouds occurred during BAECC campaign. Data is binned by liquid water path and cloud depth. (b) Re as a function LWP colored by CCN.

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REFERENCES


A CONTINUOUS FLOW DIFFUSION CHAMBER STUDY OF SEA SALT PARTICLES ACTING AS CLOUD SEEDS: DELIQUESCENCE; ICE NUCLEATION AND SUBLIMATION

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Keywords: ice nucleation, deliquescence, continuous flow diffusion chamber, sea salt

INTRODUCTION

Sea Salt Aerosols (SSA), mainly composed by NaCl, are abundant in the atmosphere, and important to the Earth’s chemistry and energy budget. However, the understanding of the roles of sea salts playing in the context of cloud formation is still poor, which is partially due to the complexity of the water-salt phase diagram. At ambient temperatures, even well below 0°C, NaCl deliquesces at sub-water saturated conditions (RH ~75%). Since the ratio of the partial pressure over ice versus super-cooled water continuously declines with decreasing temperatures, it is interesting to consider if SSA/NaCl continues to deliquesce under a super-saturated condition of ice, or if particles act as depositional ice nuclei when critical supersaturation is reached (i.e., below -29°C the equilibrium pressure over ice becomes lower than 75% RH of super-cooled water.). Some recent studies using different experimental techniques suggest hydrated NaCl and simulated sea salt might deliquesce down to a wide temperature span of -35°C to -44°C, and below that deposition freezing becomes possible1-3.

Deliquesced droplets could subsequently freeze via the immersion or homogenous freezing mechanism. After the droplets or ice particles are formed, it is also interesting to consider how the different processes may influence physical properties after evaporation or sublimation. This data is important for climate modeling that includes bromine burst observed in Antarctica, which is hypothesized to be relevant to the sublimation of blowing snow particles4.

METHODS

In this study we use a SPectrometer for Ice Nuclei (SPIN; DMT, Inc., Boulder, CO) to perform a series of experiments over a wide range of temperature and RH conditions to quantify deliquescence, droplet breakthrough and ice nucleation. The formation of droplets and ice particles is detected by an advanced Optical Particle Counter (OPC) and the liquid/solid phases are distinguished by a machine learning method based on laser scattering and polarization data. Using an atomizer, four different sea salt samples are generated: pure NaCl and MgCl2 solutions, synthetic sea water, and collected samples of sea water. Downstream of the SPIN chamber, a Pumped Counterflow Virtual Impactor (PCVI) is connected to separate the activated ice particles/large droplets to allow them undergo complete evaporation and sublimation.

CONCLUSIONS

The particle size distributions are measured and compared to those upstream of SPIN to determine the effects of the ice/droplet nucleation process on the aerosol physical parameters.
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REFERENCES


CLIMATIC IMPLICATIONS OF PARTICULATE MATTER: DIMMING OR BRIGHTENING?

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Keywords: particulate matter, climate, sulphate, global radiation.

INTRODUCTION

Atmospheric particulate matter influences the Earth’s radiative budget directly by scattering and absorbing incoming solar radiation and indirectly by influencing cloud micro-physics and radiative properties (Twomey, 1974). Regional haze layers reflecting solar radiation were typically attributed to particulate matter pollution resulting in global dimming (Andreae et al., 2005). Over the past 40-50 years both global dimming and global brightening have been observed, despite concurrent increase in temperature, and invariably attributed to air pollution (Wild et al., 2004). However, in the last three decades, pollution levels in Europe and North America have gradually decreased due to effective clean air policies and establishment of regulatory monitoring networks. Atmospheric aerosols have a strong cooling effect and have been significantly offsetting global warming by greenhouse gases, but recently reduced pollution has been tentatively related to regional brightening over the Northeast Atlantic (O’Dowd et al., 2013) based on a decade long measurements at Mace Head. As air pollution control policies are projected to reduce particulate sulphate levels by 30-70% and black carbon by 15-50% by 2050, the cooling potential of atmospheric particulates will decrease as well. It is, therefore, vital to understand the above effects as the reduced cooling (increased global warming) will have a negative impact on human health although improved air quality would be beneficial. Long-term monitoring data revealed that the above projections hold, showing 70% decrease in sulphate levels at Mace Head in the last decade alone (O’Dowd et al., ICNAA2017). A more extensive study has been undertaken including long-term data from Valentia observatory and several stations in Europe spanning the whole continent.

METHODS

Inorganic chemical composition of PM2.5 and/or PM10 samples has been continuously observed at Valentia since 1980 and Mace Head since 2001 on a daily basis. Particulate matter samples for the analysis of inorganic ions including sulphate were collected with PM10 size selective inlet at 2m above ground level at Valentia. Particulate matter and sulphur dioxide samples were collected using sequentially mounted untreated and impregnated Whatman 40 filters - a 2-stage filter pack method approved at EMEP sites. The measurement programme at Mace Head started in 2001 on a 10 m tower using PM10 size selective inlet and PTFE filters for inorganic ion analysis only. Valentia samples were analysed by the Thorin method from 1980 until 1992 and by ion chromatography since 1992. Mace Head samples were analysed only using ion chromatography for a set of inorganic ions including sulphate. Regular filter blanks were collected at both locations. Sample frequency was daily at both locations and yearly average concentrations were produced by taking arithmetic average of daily values.

Concurrently, global solar radiation (combined diffuse and direct) measurements were undertaken at both locations. Both stations in Ireland are located on the west boundary of Europe (and west coast of
Ireland) and are exposed to westerly air masses from the North Atlantic approximately 50-60% of the time (Rinaldi et al., 2009). The rest of 40-50% are the air masses of varying degree of pollution from Europe.

In order to obtain a regional perspective several EMEP stations in Europe spanning the whole European continent were evaluated for similar trends: Hyytiala (Finland), Karvåtn and Birkenes (Norway), Preila (Lithuania), Melpitz (Germany), Ispra and Montelibretti (Italy). The selection of station was based on availability of long-term sulphate data concurrent with global radiation data and the strategy of covering as much of the European continent as possible. Particulate sulphate measurement methods at above stations were generally similar to the ones used at Valentia and Mace Head although there were slight differences in either sampling height or size-selective inlet which would have insignificant impact on nss-sulphate concentrations due to the fact that non-sea-salt sulphate is largely limited to submicron particle range.

RESULTS

Concomitant with the decadal scale reduction in nss-sulphate mass an increase in surface insolation (combined diffuse and direct) was measured at Mace Head during 2003-2011 (O'Dowd et al., 2013). The annual average radiation increased from 108 Wm\(^{-2}\) in 2003 to 125 Wm\(^{-2}\) in 2010 and this increase, of ~20%, was strongly correlated to the decrease in nss-sulphate mass. Similar declining trends were seen in nitrate and ammonium aerosol, both of which were highly correlated to nss-sulphate mass (r=0.94) for both cases, and ammonium was even more correlated with nitrate (r=0.98), again reaffirming the anthropogenic nature of the sulphate aerosol. Surface insolation was also highly correlated with the combined sulphate, nitrate and ammonium PM10 mass concentration. This trend, although statistically significant, was potentially questionable, due to the rapidly increasing global radiation levels which is difficult to reconcile with the generally accepted radiative forcing of particulate matter, particularly direct and indirect radiative forcing.

Data from the Valentia station, over the period of 35 years, is presented in Figure 1 along with the data from Mace Head over the much shorter period.

![Figure 1. A combined global solar radiation relationship to PM10 sulphate mass at Valentia and Mace Head over the period of 1980-2015: (circles) Valentia data; (open stars) Mace Head. Only Valentia were fitted by linear regression with corresponding correlation coefficient.](attachment:image.png)
Although the relationship between the global radiation and sulphate (sulphur) was again statistically significant with a correlation coefficient of $-0.43$ ($P<0.01$) the observed trend was significantly shallower than the one presented by O’Dowd et al. (2013). The increase in global radiation was approximately $7 \text{ Wm}^{-2}$ over 35 years during which period sulphate concentrations in PM10 samples decreased about 7 times from approximately $3 \mu g \text{ m}^{-3}$ to $0.5 \mu g \text{ m}^{-3}$. Mace Head data presented alongside the Valentia data suggest a similar albeit slightly steeper trend. It worth noting that despite further decreasing sulphate concentrations global solar radiation turned into decreasing trend recently (after 2010) implying a more convoluted relationship. The linear regression presented in Figure 1 can explain about 20% of the variance in the dataset. Consequently, very rapid change presented in O’Dowd et al. (2013) most likely was a combination of pollution related brightening together with the changes of cloud cover due to changing pattern of global circulation tentatively attributed to global warming. One of the primary suspects of a hidden relationship may be the North Atlantic Oscillation changing the dominant circulation patterns, particularly the polar jet.

In order to understand the underlying effects it was important to look into the wider European region. A compilation of data from the established monitoring stations in Europe has been carried out and the data were thoroughly examined for sulphate-radiation relationship. Approximately a decade long dataset of global radiation and sulphate data have been gathered from 8 stations around Europe (Finland, Lithuania, Norway, Germany, Italy and Ireland). Two stations (Lithuania and Birkenes) resemble a similar pattern to the one found at Mace Head and Valentia (Figure 1) albeit with a shallower slope. The other five stations exhibited an opposite trend where reducing sulphate concentrations were concurrent with reducing global radiation. Interestingly, Mace Head, Lithuanian and Norwegian stations were all coastal, whereas the stations exhibiting the opposite trend to Mace Head and Valentia were all continental (stations in Italy, Germany and Finland). No clear pattern has been observed with regard to the magnitude of sulphate concentrations disputing the findings and conclusions based on Mace Head data alone.

CONCLUSIONS

The 35 years of air pollution abatement strategies have resulted in dramatic decrease of sulphate concentrations at a background location in Valentia (Ireland) where a reduction of an excess of 70% has been observed. The concurrent trend was also observed at Mace Head location as well as across the European continent. Sulphate is a ubiquitous pollutant tracing closely particulate matter mass. This very significant decrease should have been accompanied by an increase in global solar radiation following the brightening phenomenon as fewer aerosol particles should scatter less of incoming solar radiation and making optically ticker and less reflective cloud layers. Instead, various relationships were obtained in different parts of Europe with coastal stations exhibiting a brightening trend while continental stations exhibiting a dimming trend. The relationship between sulphate and global radiation was statistically significant at most locations in Europe suggesting that reducing pollution levels are indeed related to radiation. However, the mechanism behind the relationships and more importantly opposite in sign at certain locations requires a more holistic approach taking into account regional and global circulation patterns which ultimately affect cloud cover and the global radiation.

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REFERENCES


50 YEARS OF ECOLOGICAL RESEARCH AND
25 YEARS OF COMPREHENSIVE ATMOSPHERE-BIOSPHERE INTERACTION STUDIES AT VÄRRIÖ RESEARCH STATION IN EASTERN LAPLAND

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Keywords: comprehensive observations, atmospheric aerosols, photosynthesis, atmosphere-biosphere interactions

BACKGROUND

Värriö research station (Petäjä et al. 2017) is located in Eastern Lapland in Finland at 68ºN in the vicinity of Russian border. The station itself is inside a strict nature reserve. The history of Värriö research station originates back to 1967. At first the research concentrated particularly on animals typical for the Finnish Lapland, such as wolverine (Pulliainen, 1968), wolf (Pulliainen, 1980, 1981) as well as their protection (Pullianen, 1982). At this time, observations of bird nesting were initiated (e.g. Pulliainen, 1977), which are still continued. Such datasets provide valuable information on the long-term climate change in the Arctic region.

In the 1980s and 1990s environmental issues, such as acidification (Kauppi et al. 1990) and radioactivity were important topics also in Värriö research station. The former was of particular interest in Värriö as intensive emissions from mining industry to the site from Kola Peninsula in a form of transboundary atmospheric pollution and acid rain. The latter was manifested by studies of the Chernobyl fallout (Raunemaa et al. 1987). These concerns raised awareness on the importance of continuous observation series to address changes both in the biosphere but also in the atmosphere. At the beginning of 1990s, construction of Station for Measuring Ecosystem – Atmosphere Relations I (SMEAR I, Hari et al. 1992) was initiated. The underlying philosophy in this work was that one needs to understand the material and energy fluxes between the biosphere and the atmosphere in order to draw conclusions on the processes leading to changes in the ecosystems (Hari et al. 2016). After promising results in Värriö, another measurement site (SMEAR II, Hari and Kulmala, 2005) was developed and constructed in Hyytiälä, southern Finland in mid-1990s. Subsequently even more sites are included in the SMEAR network in Finland (Järvi et al. 2009, Leskinen et al. 2009, in Estonia (Noe et al. 2016) and in China (Ding et al. 2013).

The aim of this work is to present a concise overview of the scientific work performed at Värriö research station, particularly concerning the biosphere-atmosphere relations based on observational data from SMEAR I.

ON SELECTED KEY FINDINGS

The key findings from SMEAR I in Värriö include the detection of secondary aerosol formation i.e. formation of atmospheric nanoparticles from gas-phase precursors (e.g. Kulmala et al. 2004, Vehkamäki et al. 2004). Although more comprehensive observations are conducted at SMEAR II in Hyytiälä, the first total aerosol number measurements in Värriö already in 1992 showed signs of the formation of aerosol particles. However, without a proper measurement of the size distribution, these occasions were not properly identified as new particle formation events. As the number size distribution measurements were
included in the capacity of the SMEAR I, the events were identified and characterized. In the clean Arctic air in Värriö, the formation rates are smaller than in SMEAR II station while the growth rates are similar. At Värriö, aerosol growth rates (GR) for the nucleation mode and formation rate of 3 nm particles (J3) vary from 1.8 nm h⁻¹ to 4.4 nm h⁻¹ and 0.07 cm⁻³s⁻¹ to 0.21 cm⁻³s⁻¹ as monthly averages calculated from the data from the events from 1992 to 2011 and 2005 to 2011, respectively (Kyrö et al. 2014). The corresponding values for SMEAR II in Hyytiälä are 2.5 nm h⁻¹ and 0.84 cm⁻³s⁻¹ for GR and J3, respectively (Nieminen et al. 2014).

The long-term data on atmospheric aerosol particle concentrations and trace gas mixing ratios in Värriö show that the transboundary transport of aerosol particles and sulfur dioxide has decreased during the 25 years of operation (Kyro et al. 2014). This is linked to decreased emissions in the Kola industrial areas in Russia.

The comprehensive observations in Värriö SMEAR I enables a thorough and integrated analysis of long ecological time series (such as start of the bird nesting), meteorological observations, photosynthesis and atmospheric composition (greenhouse gases, fluxes, aerosol particles and trace gas concentrations). This will increase our understanding on the responses of the biosphere to global warming.

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REFERENCES


EVIDENCE FOR THE FORMATION OF DMS-DERIVED AEROSOLS DURING ARCTIC PHYTOPLANKTON BLOOMS

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Keywords: Dimethyl Sulfide, Sulfur Isotope, Methanesulfonic Acid, Aerosols, Phytoplankton

INTRODUCTION

Over the past 3 decades, DMS emissions from the upper ocean have been considerably studied because there may be a direct association between marine biota and climate change (Charlson et al., 1987). However, the contribution of oceanic DMS emission to the formation of aerosol particles and CCN remains poorly quantified. In the absence of this knowledge, in particular a lack of observational evidence for a direct association between DMS production and the formation and growth of aerosol particles in the marine boundary layer, doubts remain as to the validity of the hypothesized feedback mechanism connecting DMS-derived aerosols to climate (Quinn and Bates, 2011). The aims of the present study were to investigate the direct association of DMS emissions with the formation of aerosol particles, and to assess the contribution of DMS to total $\text{SO}_4^{2-}$ aerosol budget. To this end we analyzed datasets of atmospheric DMS mixing ratio, aerosol particle size distributions, and aerosol chemical composition measured at Ny-Ålesund (Svalbard; 78.5 °N, 11.8°E) in April and May 2015. To address the second aim we analyzed the MSA concentration (formed exclusively from the photo-oxidation of DMS) and the stable S isotope composition of aerosol particles.

METHODS

The atmospheric DMS mixing ratio was measured at 1–2 h intervals on the Zeppelin observatory, which is located at an elevation of 474 m above sea level (m.a.s.l) and 2 km south and southwest of Ny-Ålesund. The measurement period (April – May) approximately covered the pre- to post-phytoplankton bloom periods. The distribution of aerosol particle sizes was measured at the Gruvebadet observatory, which is approximately 1 km southwest of Ny-Ålesund and approximately 60 m.a.s.l. Both a differential mobility analyzer and a condensation particle counter continuously measured the occurrence and distribution of two discrete small particle size ranges (3–60 nm and 10–500 nm in differential mobility equivalent diameter), and an aerodynamic particle sizer (APS) analyzed larger particles in the range 0.5–20 μm in diameter. A high volume air sampler equipped with a PM2.5 impactor (collecting particles < 2.5 μm in aerodynamic equivalent diameter) was used for collection of aerosol samples. The sampler was mounted on the roof of the Gruvebadet observatory, and sampled particles every 3 days between 9 April and 20 May 2015, and later measured concentrations of major ions including MSA and the stable S isotope composition on a quartz filter.

RESULT AND CONCLUSIONS

Measurements of atmospheric DMS mixing ratios, size distribution of aerosol particles and chemical composition of aerosol particles showed distinct patterns during periods of Arctic haze (April) and phytoplankton blooms (May). Specifically, during the phytoplankton bloom period the contribution of DMS-derived $\text{SO}_4^{2-}$ to the total aerosol $\text{SO}_4^{2-}$ increased by 7-fold compared with that during the proceeding Arctic haze period, accounting for up to 70% of fine $\text{SO}_4^{2-}$ particles (< 2.5 μm in diameter).
The results also showed that a sharp increase in the atmospheric DMS mixing ratio during Arctic phytoplankton bloom events was directly associated with the formation of sub-micrometer SO$_4^{2-}$ aerosols, and their subsequent growth to climate-relevant particles (Fig. 1). Most importantly, two independent estimates of the formation of DMS-derived SO$_4^{2-}$ aerosols, calculated using the stable S isotope ratio and non-sea-salt SO$_4^{2-}$/MSA ratio, respectively, were in close agreement, providing compelling evidence that the contribution of biogenic DMS to the formation of aerosol particles was substantial during the Arctic phytoplankton bloom period. This study provided the observational evidence confirming direct relationships between an increase in atmospheric DMS and the formation and growth of aerosol particles, and also an increase in the total mass concentration of nss-SO$_4^{2-}$ during Arctic phytoplankton blooms. Concurrent measurements of a suite of parameters (DMS, satellite-derived phytoplankton biomass, concentration and chemical composition of particles) supported the assertion that oceanic emission of DMS significantly affects the properties of sub-micrometer particles in the Arctic atmosphere.

Figure 1. Spectral plot of number size distribution (dN/dlogDp) as a function of particle diameter (Dp, 10–500 nm) and year day during April and May 2015. The black line represents the concentration of biogenic SO$_4^{2-}$.

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REFERENCES


MULTIPLE SCATTERING CORRECTION FOR DIFFERENT AETHALOMETER CORRECTION ALGORITHMS AT THE SMEAR II STATION

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Keywords: AEROSOL, OPTICAL PROPERTIES, AETHALOMETER.

INTRODUCTION

Aerosol particles have a direct impact on the climate since they scatter and absorb radiation from the sun. Compared to greenhouse gases, the estimated radiative forcing of aerosol particles has a large uncertainty because of the large variability of aerosol particles both in time and space (Boucher et al., 2013). Measurements of the optical properties of aerosol particles are needed to determine the direct effect of aerosol particles on climate. The absorption coefficient of aerosol particles is commonly measured with filter-based instruments. Collecting aerosol particles on a filter however causes systematic error to the measurements because the filter material also interacts with radiation. Also the gradually increasing filter loading is causing an error to the measurements. The biases caused by these factors are taken into account in various correction algorithms. In this study a multiple scattering correction factor was defined for different aethalometer correction algorithms at the SMEAR II station.

METHODS

The measurements presented in this study were conducted at the SMEAR II station during 19.06.2013 - 16.10.2016. The station is located in Hyytiälä, Southern Finland (61°51′N, 24°17′E) and it represents conditions of a boreal forest. Measurements with an aethalometer (Magee Scientific model AE-31), an integrating nephelometer (TSI model 3563) and a Multi-Angle Absorption Photometer (MAAP, Thermo model 5012) were used.

The aethalometer measures the attenuation coefficient ($\sigma_{ATN,aeth}$) of aerosol particles at seven wavelengths (370, 470, 520, 590, 660, 880 and 950 nm). To obtain the absorption coefficient ($\sigma_{abs,aeth}$), $\sigma_{ATN,aeth}$ needs to be corrected for the multiple scattering of the filter material ($C_{ref}$). Also a correction for the increasing filter loading ($R$) is needed

$$\sigma_{abs,aeth} = \frac{\sigma_{ATN}}{R(AN)C_{ref}}$$

The filter loading correction depends on the attenuation (ATN) of the filter. There are several filter loading correction algorithms, e.g., those developed by Weingartner et al., (2003); Arnott et al., (2005); Virkkula et al., (2007) and Collaud Coen et al., (2010), which were used in this study. Some of the correction algorithms also need information of the scattering coefficient ($\sigma_{scat}$) of aerosol particles, which was measured at three wavelengths (450, 550 and 700 nm) with an integrating nephelometer. The truncation correction presented by Anderson and Ogren (1998) was applied for the measured $\sigma_{scat}$. 
$C_{\text{ref}}$ is determined by correcting $\sigma_{\text{ATN},\text{aeth}}$ with $R(\text{ATN})$ and comparing it to a reference absorption coefficient $\sigma_{\text{abs},\text{ref}}$

$$C_{\text{ref}} = \frac{\sigma_{\text{ATN}}}{R(\text{ATN}) \sigma_{\text{abs},\text{ref}}}$$

In this study $\sigma_{\text{abs},\text{ref}}$ was measured by MAAP. Also MAAP measures $\sigma_{\text{abs}}$ by collecting particles on a filter but it also measures the backscattering of radiation from the filter and the collected sample. With the backscattering measurements, the errors caused by the filter can be corrected. In the comparison the aethalometer measurements at the wavelength of 660 nm were used, since it is the closest wavelength to the wavelength of the MAAP measurements. MAAP measures $\sigma_{\text{abs},\text{ref}}$ at wavelength of 637 nm. In the correction algorithm defined by Weingartner et al. (2003) $C_{\text{ref}}$ was defined only for a clean filter (ATN < 10). In the correction algorithm by Arnott et al. (2005) $R$ depends on cumulative $\sigma_{\text{abs,aeth}}$ and $\sigma_{\text{abs,aeth}}$, so $C_{\text{ref}}$ was defined to each filter by an iterative algorithm. For all the other correction algorithms $C_{\text{ref}}$ was defined from 1 hour averaged data.

CONCLUSIONS

The averages, medians and standard deviations of $C_{\text{ref}}$ for different correction algorithms are presented in Table 1. The average values of $C_{\text{ref}}$ between different correction algorithms have some variation. The largest value is $C_{\text{Weingartner}} = 3.42 \pm 0.67$ and the smallest value is $C_{\text{CollaudCoen}} = 3.04 \pm 0.67$ but the difference is not large when the standard deviation is considered. The $C_{\text{ref}}$ values defined at the SMEAR II station were compared to the $C_{\text{ref}}$ values defined by Collaud Coen et al. (2010) for different kinds of environments. The $C_{\text{ref}}$ values at the SMEAR II were clearly higher than those that Collaud Coen et al. (2010) had measured at stations located in very clean environments (Jungfraujoch and Hohenpeissenberg). Correspondingly Collaud Coen et al. (2010) had measured higher $C_{\text{ref}}$ in a more urban environment (Cabauw) than what was defined for SMEAR II station.

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Median</th>
<th>Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{uncorr}}$</td>
<td>3.21</td>
<td>3.14</td>
<td>0.71</td>
</tr>
<tr>
<td>$C_{\text{Weingartner}}$</td>
<td>3.42</td>
<td>3.34</td>
<td>0.67</td>
</tr>
<tr>
<td>$C_{\text{Arnott}}$</td>
<td>3.23</td>
<td>3.19</td>
<td>0.67</td>
</tr>
<tr>
<td>$C_{\text{Virkkula}}$</td>
<td>3.41</td>
<td>3.32</td>
<td>0.71</td>
</tr>
<tr>
<td>$C_{\text{CollaudCoen}}$</td>
<td>3.04</td>
<td>2.97</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 1. The average, median and standard deviation of $C_{\text{ref}}$ for different correction algorithms.

The seasonal variation of $C_{\text{ref}}$ (Figure 1) shows that it obviously does not depend on the filter material only. The annual variation is similar between all the different correction algorithms. The monthly median values are below the average during winter and early spring (Jan - Apr) and during summer (Jun - Oct) the monthly medians are higher than the average. Neglecting the annual variation of $C_{\text{ref}}$, the measured absorption coefficient is overestimated during summer and underestimated during winter and spring. There’s no confirmed explanation for the variation of $C_{\text{ref}}$. Weingartner et al. (2003) thought that condensing material on the filter and collected liquid particles on the filter might change the optical properties of the filter fibres causing the variation of $C_{\text{ref}}$. Collaud Coen et al. (2010) suggested that the $C_{\text{ref}}$ might depend on the single scattering albedo of aerosol particles.
Figure 1. Annual variation of $C_{ref}$ for different correction algorithms. Edges of the boxes represent 25th and 75th percentiles, the orange line in middle is the median and the whiskers represent 10th and 90th percentiles. The grey line is the median value of $C_{ref}$ derived for each correction algorithm.

ACKNOWLEDGEMENTS

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REFERENCES


SENSITIVITY ON THE OPTICAL PROPERTIES FOR HULIS AEROSOL AT ANMYEON ISLAND, KOREA

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Keywords: humic-like substances (HULIS), Optical Properties, Radiative Forcing, Hygroscopic Growth Factor, Light Absorption

INTRODUCTION

Characterization of water soluble organic carbon (WSOC) is important because it is believed to act as cloud condensation nuclei (CCN). Among WSOC, a substantial fraction of WSOC is known to be of humic-like substances (HULIS) (Saxena and Hildemann, 1996). In this study, sensitivity of the optical properties of carbonaceous aerosol, especially HULIS, are investigated based on a one-year measurement of particulate matter that is less than or equal to 2.5 μm in aerodynamic diameter (PM2.5) at a Global Atmospheric Watch (GAW) station in South Korea. The extinction, absorption coefficient, and radiative forcing (RF) are calculated from the analysis data of water soluble (WSOC) and insoluble (WISOC) organic aerosols, elemental carbon (EC), and HULIS. Sensitivity of the optical properties on the variations of refractive index, hygroscopicity, and light absorption properties of HULIS and the polydispersity of organic aerosols are studied.

MEASUREMENT DATA

The study site was Anmyeon Island (36.32°N, 126.19°E, altitude 45.7 m) located on the western coast of Korea. A total of fifty nine daily PM2.5 samples were collected from June 2015 to May 2016 for every 6th day. Among them, thirty five HULIS samples were available from July 2015 to April 2016 and used in this study after quality assurance/quality control (QA/QC) procedure. OC and EC were analyzed by a thermal/optical carbon aerosol analyzer (OCEC Model 5L, Sunset Laboratory, Forest Grove, OR) applying on the NIOSH (National Institute of Occupational Safety and Health) Method. For WSOC and HULIS analysis, PM2.5 samples were extracted with distilled de-ionized water (DDW, 18.2 MΩ) by ultrasonification. The extracts were divided two fractions and one is applied for WSOC analysis and the other is used HULIS-C extraction by SPE (solid phase extraction) cartridge (OasisHLB, 30 mm, 60 mg/cartridge, Waters, USA). Both WSOC and HULIS-C were analyzed using a TOC (total organic carbon) analyzer (Sievers M9, General Electric power & water Analytical Instruments, USA). Figure 1 shows the variation of the concentrations and relative fractions of WSOC, WISOC, EC, and HULIS for daily basis. HULIS accounted for 23–76% of the total carbonaceous aerosol (TCA) mass concentration during the sampling period. WISOC and WSOC excluding HULIS (residual WSOC = WSOC - HULIS) accounted for 13–64% and 1–39% of the TCA, respectively.

RESULTS: OPTICAL PROPERTIES OF HULIS AEROSOL

In this study, the optical properties carbonaceous aerosol were calculated. The hygroscopicity, light absorption, size distribution, and chemical composition were considered. The mass concentration of EC, WSOC, WISOC, and HULIS of PM2.5, were given as input data. Lognormal aerosol size distribution and the species densities and refractive indices of externally mixed organic aerosols were assumed in this study (Wex et al., 2002b; Mallet et al., 2004). The aerosols in the atmosphere are distributed in a broad
range of sizes. Different aerosol size distributions have different optical properties due to the variation of extinction coefficient with aerosol size. In this study, the size distribution of ambient polydispersed aerosols is presented using a lognormal distribution function (Jung et al., 2015):

\[ n(\ln d_p) = \frac{N}{\sqrt{2\pi \ln \sigma_g}} \exp \left[ -\frac{\ln^2(d_p / d_g)}{2\ln^2 \sigma_g} \right] \]  

(1)

where, \(d_p\) is the diameter of the particle, \(d_g\) is the geometric mean diameter, \(\sigma_g\) is the geometric standard deviation, and \(N\) is the total number concentration.

Figure 1. Variation of the concentrations of carbonaceous species in PM2.5 measured at Anmyeon station.

Figure 2 shows the seasonal variation of extinction and the absorption coefficients for each carbonaceous component. The maximum and minimum extinction and absorption coefficients are calculated in the range of geometric mean diameter from 0.1 to 1 \(\mu\)m and geometric standard deviation from 1.1 to 2.0. The IRI of 0.006–0.3 was considered for HULIS aerosols. As Fig. 2 shows, the seasonal extinction coefficient of HULIS ranges from 0.52 \(\text{Mm}^{-1}\) to 20.86 \(\text{Mm}^{-1}\). EC and HULIS are dominant contributors to the absorption coefficient. The absorption coefficient of EC ranges from 0.11 to 3.04 \(\text{Mm}^{-1}\). On the other hand, the absorption coefficient of HULIS ranges from 0.09 \(\text{Mm}^{-1}\) to 11.64 \(\text{Mm}^{-1}\). EC contributes 18%-40% of the TCA to the absorption coefficient. However, HULIS shows a wider range of contribution. The comparison also shows that the contribution of HULIS dominates the absorption properties of aerosol over EC in this measurement period at Anmyeon Island. It should also be noted that the contribution of the absorption coefficients of WISOC and other WSOC increase when the contribution of HULIS aerosol decreases.

<table>
<thead>
<tr>
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<th>Refractive index (550 nm)</th>
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<tbody>
<tr>
<td>EC</td>
<td>1.9-0.66i</td>
</tr>
<tr>
<td>HULIS</td>
<td>1.595-0.006i ~ 1.595-0.3i</td>
</tr>
<tr>
<td>WSOC</td>
<td>1.53-0.006i</td>
</tr>
<tr>
<td>WISOC</td>
<td>1.53-0.006i</td>
</tr>
</tbody>
</table>
Figure 2. Seasonal variation of extinction and absorption coefficients for each carbonaceous component \((0.1<d_a<1, 1.1<\sigma_s<2.0, 0.006<HULIS\text{ imaginary refractive index}<0.3)\).

CONCLUSIONS

In this study, the optical properties of carbonaceous aerosol including HULIS, were investigated based on PM2.5 data measured over one year in Amnyeon Island, Korea. The extinction, absorption coefficient, and RF were calculated, with particular focus on the light absorption properties of HULIS. The polydispersity effects on the optical properties were also considered by assuming lognormal size distribution. The results showed that the imaginary refractive index of HULIS plays an important role in estimating the aerosol optical properties. This study also shows that the size distribution is important parameter in estimating the aerosol optical properties.

REFERENCES


TRANSBOUNDARY TRANSPORT OF ANTHROPOGENIC SULFUR IN PM$_{2.5}$ AT A COASTAL SITE IN THE SEA OF JAPAN

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Keywords: PM$_{2.5}$, sulfate isotopic ratio, transboundary transport, Northeast Asia

INTRODUCTION

In January 2013, extremely high mass concentrations of particulate matter (PM$_{2.5}$) were observed in Beijing, China. In Japan, which is located downwind of the prevailing winds drawn from the Asian continent, high concentrations of PM$_{2.5}$ were observed at several locations and times, the values exceeding the target value of environmental standard on daily average in Japan (35 µg m$^{-3}$ per day). Based on a model simulation, it is clear that high mass concentrations of PM$_{2.5}$ for this event observed in Japan were the result of transboundary transport from the Asian continent under stable atmospheric conditions (Uno et al., 2013). Because of adverse effects on human health, knowledge of the temporal and spatial variations of PM$_{2.5}$ mass concentrations in downwind regions as well as the source regions are of great interest. The sulfur isotopic ratio ($\delta^{34}S$) is regarded as useful chemical tracers to investigate the source contributions of sulfate in aerosols and precipitation, because the values are different among the sources. The region facing to the Sea of Japan, located on the leeward of the Asian continent, is strongly influenced by transboundary transport of anthropogenic pollutants emitted from the Asian continent under the westerly wind (Inomata et al., 2016). In this study, daily observations of $\delta^{34}S$ in PM$_{2.5}$ were carried out the Niigata-Maki site facing to the Sea of Japan during the intensive monitoring periods from 2013 to 2015. In order to evaluate the contribution of transboundary transport of anthropogenic sulfur, horizontal distribution of $\delta^{34}S$ in coal in the Northeast Asia is statistically investigated by optimal interpolation analysis. By using the average $\delta^{34}S$ value in coal corresponding the air mass transport region in the Northeast Asia, contribution of transboundary transport of anthropogenic sulfur in PM$_{2.5}$ is evaluated.

METHODS

Airborne particulate samples were collected at the National Niigata-Maki Acid Deposition Monitoring station (hereafter Niigata-Maki, longitude 138.85°E, latitude 37.81°N), which is located facing to the Sea of Japan. A high volume air sampler (KIMOTO Model 120F, SHIBATA HV-1000F) with PM$_{2.5}$ impacter (Tokyo Dylec Co., HV12.5, Kaneyasu, 2010) was used to sampling. Intensive sampling was performed in four seasons from 2013 to 2015 (13–20 May 2013, 29 July–5 August 2013, 28 October–5 November 2013 and 27 January 2014–3 February 2014, 8–22 May 2014, 23 July–6 August 2014, 22 October–4 November 2014 and 21 January 2015–4 February 2015, 7–21 May 2015, 22 July–5 August 2015, 22 October–4 November 2015). The airborne particulate samples were collected over a 24 hr period (12:00–12:00 local time). PM$_{2.5}$ samples were collected on a quartz fiber filter (2500 QAT-UP, Pall Science Co. Ltd.) after the coarse particles (diameter > 2.5 µm), which were collected on a separate quartz fiber filter (HV-SF, Pall Science Co. Ltd.). Filter samples for PM$_{2.5}$ and coarse particles were subjected to ultrasonic extraction with MilliQ water to extract water soluble ion species (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$). The concentrations of water soluble ions were measured by ion chromatography (anions, ICS-1000 column; cations, DX-120 column; DIONEX Co. Ltd.). For measurement of $\delta^{34}S$, filter was finely cut, following then, the sample was subjected twice to ultrasonic extraction with 100–200 mL MilliQ water for
30 minutes. The combined extracts containing SO$_4^{2-}$ were then evaporated to less than 100 mL and added BaCl$_2$ solution so as to precipitate BaSO$_4$ under acidic conditions. The BaSO$_4$ precipitate was then collected by filtration (5C filter, Advantec Co Ltd.), whereupon the sample was burned and ashed by a gas burner and then by electric oven at 800 °C for 2 hr. The recovery of BaSO$_4$ was between 70–90%, depending on the abundance of SO$_4^{2-}$. The BaSO$_4$ samples were analyzed by stable isotope mass spectrometry (Delta Plus, Thermo Co. Ltd.).

The $\delta^{34}$S was expressed in conventional notation as follows:

$$\delta^{34}S_{(\%)} = \left( \frac{\delta^{34}S_{(\text{sample})}}{\delta^{34}S_{(\text{CDT})}} - 1 \right) \times 1000$$  

where X and CTD stand for a sample and Canyon Diablo Troilite (CDT) as standard, respectively. The accuracy of sulfur isotopic analysis was ± 0.14‰. The $\delta^{34}$S of nssSO$_4^{2-}$ ($\delta^{34}$S$_{\text{nss}}$) was calculated by using the $\delta^{34}$S$_{\text{nss}}$ value in seawater (+20.3‰) and the ratio of SO$_4^{2-}$/Na$^+$ in seawater (0.251).

The relative contribution of different sulfur sources to sulfate in PM$_{2.5}$ was estimated. The sources of sulfate in PM$_{2.5}$ were assumed to be transboundary transport, sea salt, and local (domestic). The simplified material balance equations are made as follows:

$$\delta^{34}S = f_{\text{TRB}} \cdot \delta^{34}S_{\text{TRB}} + f_{\text{ss}} \cdot \delta^{34}S_{\text{ss}} + f_{\text{LOC}} \cdot \delta^{34}S_{\text{LOC}}$$  

(2)

$$f_{\text{TRB}} + f_{\text{ss}} + f_{\text{LOC}} = 1$$  

(3)

$$f_{\text{ss}} = \frac{(\text{Na}^+)_\text{obs} \times (\text{SO}_4^{2-}/\text{Na}^+)_\text{obs}}{(\text{SO}_4^{2-})_\text{obs}}$$  

(4)

where TRB, SS, LOC represent the transboundary transport of anthropogenic sources from the Asian continent, sea salt, and local (domestic) anthropogenic sources, respectively; $f$ indicates the fraction of each contribution to the $\delta^{34}$S value; $\delta^{34}$S$_{\text{TRB}}$ assumes that the average value for $\delta^{34}$S originated from coal in the area where the air mass was transported for a particular day. The $\delta^{34}$S$_{\text{nss}}$ value was +20.3‰ based on the $\delta^{34}$S value in sea salt (Rees, C.E. et al., 1978). The $\delta^{34}$S$_{\text{LOC}}$ value was assumed to be –2.7‰ based on the combustion experiment of oil used in the observation region (Ohizumi et al., 1997). The $\delta^{34}$S$_{\text{TRB}}$ was estimated by the distribution of the $\delta^{34}$S in coal in Northeast Asia, where the air mass transported region by backward trajectory analysis.

CONCLUSIONS

The $\delta^{34}$S$_{\text{nss}}$ in PM$_{2.5}$ showed a seasonal variation with relatively higher values being observed in winter (2.3–6.2‰) compared with values in the other seasons (1.0–4.2‰ in spring, -0.1–4.5‰ in summer, 1.3–5.75‰ in autumn) in the intensive sampling from 2013 to 2015.

![Figure 1. Box plots of $\delta^{34}$S$_{\text{nss}}$ based on the air mass classifications (TRB, Direct Transboundary air mass transport after leaving the Asian Continent; DOM, the air mass transported over Japan after leaving the Asian Continent; NPO, the air mass transported from the North Pacific Ocean) for the four seasons. The lower boundary of the box plot indicates the 25th percentile. The line within the box marks the median and the upper boundary of the box plot indicates the 75th percentile. The line above the box plot refers to the 90th percentile and the line below the box represents the 10th percentile.](image-url)
These data were classified by using the air mass transport routes. Figure 1 shows the boxplot of $\delta^{34}S_{\text{ins}}$ in PM$_{2.5}$ classified with air mass transport route: directly transported air mass after leaving the Asian continent (TRB), the air mass transported over the Japanese islands after leaving the Asian continent (including domestic sources; DOM), and the air mass transported over the Pacific Ocean and the Japanese islands in summer (NPO). It was found that the $\delta^{34}S_{\text{ins}}$ values for TRB (3.9±0.1‰, 2.1-6.2‰) are higher than those for DOM (3.1±1.0‰, 1.0-5.8‰). The $\delta^{34}S_{\text{ins}}$ values for TRB are close to the values in aerosol observed in northern China (Mukai et al., 2001). On the other hand, it was reported that $\delta^{34}S$ in sulfate emitted from Japan was relatively low because the $\text{SO}_4^{2-}$ in Japan are dominantly emitted from oil combustion (Sakata et al., 2013). The lower $\delta^{34}S_{\text{ins}}$ in the air mass transported over the Japanese islands arriving over the site (DOM) are resulting with mixing of the emissions from the Japanese islands and the transboundary transported $\text{SO}_4^{2-}$ in PM$_{2.5}$. Therefore, relatively higher values in TRB compared with DOM are due to the large contribution from the anthropogenic sources, mainly coal combustion, in the Asian continent. The $\delta^{34}S_{\text{ins}}$ values (2.0±1.2‰, -0.1-3.8‰) for NPO were relatively lower to those for DOM. Considering that the air mass classified into NPO are not transported over the Asian continent before arriving to the monitoring site, $\text{SO}_4^{2-}$ are strongly affected by domestic sources, Japan.

The relative contribution of different sulfur sources to sulfate in PM$_{2.5}$ was estimated by using the mass balance model (eq. 2-4). Figure 2 shows the time variation of $\text{SO}_4^{2-}$ concentrations, sulfur isotopic ratio, and relative contribution from three sources. The $\text{SO}_4^{2-}$ concentrations were varied from 0.09 to 20.2 µg m$^{-3}$. The higher $\text{SO}_4^{2-}$ concentrations in spring 2013 are due to the transport of the Asian dust according to the Lidar observations (http://www.arl.noaa.gov/HYSPLIT_info.php). The higher concentrations of $\text{SO}_4^{2-}$ were also observed in summer 2015.

Figure 2 (a) Daily variations of $\text{SO}_4^{2-}$ concentrations for various sources (sea salt, transboundary transport, and local emissions (anthropogenic, biogenic and volcanic)) and $\delta^{34}S_{\text{ins}}$ in sulfate ions in PM$_{2.5}$ at the Niigata-Maki monitoring site. (b) Relative contribution from each sulfur source.
Considering that the air mass was transported over the Japanese islands or Korean Peninsula during this period, the higher SO$_4^{2-}$ would be resulted by the secondary production during the transport. The largest contribution to sulfate was transboundary transport (TRB), followed by including domestic sources (DOM), and then sea salt. The relative contribution of transboundary transport was 39–75% in spring (2013), 51–99% in summer (2013), 44–73% in autumn (2013), and 53–81% in winter (2014), 23–69% in spring (2014), 45–71% in summer (2014), 37–71% in autumn (2014), 45–82% in winter (2015), 43–89% in spring (2015), 37–71% in summer (2015), 19–80% in autumn (2015). The relative contribution of coal combustion, in other words emission from the Asian continent, was tended to be high in the TRB air mass. It is also noted that the relative contribution from DOM in summer 2015 are more than 60%. These results suggest that PM$_{2.5}$ emitted from the Asian continent are modified during transboundary transport and these are strongly affected by the meteorological conditions.

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REFERENCES

Inomata, Y., T. Ohizumi, N. Take and K. Sato (2016) Transboundary transport of anthropogenic sulfur in PM$_{2.5}$ at a coastal site in the Sea of Japan as studied by sulfur isotopic ratio measurement, Sci. Total. Environ. 553, 617.


A STUDY OF THE SEASONAL VARIATIONS IN SPECTRAL DIFFUSE AND DIRECT BEAM SOLAR IRRADIANCE OVER DELHI

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Abstract

Spectral distribution of global and direct solar irradiance has been studied over Delhi by using ASD field spectroradiometer. The impact of atmospheric constituents and aerosol on spectral composition of irradiance has been measured in cloud free conditions. Atmospheric turbidity modifies incoming global and direct and diffuse-to-direct irradiance ratio. Ratios ($E_{d}/E_{b}$) between irradiance can be use as a function to measure effect of the air mass or solar zenith angle on incoming solar irradiance is examined. The $E_{d}/E_{b}$ diffuse-to-direct-irradiance ratios decrease sharply with wavelength and exponential curves in the form $E_{d}/E_{b} = a\lambda^{-b}$ can be fitted with a great accuracy. These curves are strongly modified by the solar spectrum distribution, especially at shorter wavelength. Pollutants level very season to season which effect incoming solar irradiance is investigated in detail and it is found that pollutants level and air mass factor are responsible for high value of diffuse ratio in winter and post monsoon season. These parameters strongly affect the scattering processes in the atmosphere and as a consequence the diffuse spectral distribution. The $E_{d}/E_{b}$ ratio, which is an indicator of the atmospheric turbidity, exhibits a strong wavelength and aerosol loading dependence. Differences are observed between different seasons under clear skies conditions. This study investigating the effect of atmospheric turbidity and air mass on ratio of solar irradiance.

Key words: irradiance, aerosol, turbidity, air mass
DESIGN AND CALIBRATION OF NON-SHEATHED BUTANOL CPC SENSITIVE TO 1 nm PARTICLES

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Keywords: CPC, butanol, detection efficiency, sub 3 nm, nanoparticles, low pressure environments.

INTRODUCTION

At the global scale, modeling tools have shown that new particle formation (NPF) by nucleation and growth can significantly contribute to the total number concentrations of aerosol particles and consequently to the number of cloud condensation nuclei (Spracklen et al. 2006). In particular, nucleation is expected to be a major contributor to the total particle number concentration at higher altitudes (in the upper troposphere) (Merikanto et al. 2009), where clouds mostly form. With the development of instruments detecting particles at the nanometer scale, NPF events have been observed in a growing number of environments, and recently detected at high altitudes with a high frequency (Venzac et al., 2008; Boulon et al. 2010, 2011; Rose et al. 2015). However, understanding the mechanisms behind the nucleation process requires that particles in the sub 3 nm range (cluster particles) be detected. But until only a few years ago, before instruments that "pre-grow" particles upstream of a regular CPC (e.g. Airmodus' Particle Size Magnifier – PSM) were released, only natural cluster ions could be detected in the natural environment.

We present here the recent development of a nano-CPC capable of detecting neutral clusters in low pressure environments such as high altitude stations and airborne platforms, while keeping the design simple.

BUTANOL NANO-CPC DESIGN

Commercial fine condensation particle counters in boosted conditions (50°C for the saturator temperature and 10°C for the condenser temperature) have recently demonstrated their ability to detect particles in the sub 3 nm range (Kangasuuma et al., 2015) with butanol as the working fluid. The main benefit of using butanol is that the final droplets are large enough to be directly detected by an optical counter, which is not the case of diethylene glycol used in PSMs. PSMs thus need a companion CPC to grow particle further, and detect them.

This high detection efficiency is obtained when the temperature difference between the saturator (Ts) and the condenser (Tc) is increased from 17°C (non boosted conditions) to 40°C (boosted conditions). The temperature setpoints of the TSI 3772 and Airmodus A20 used in Kangasuuma’s study are limited to 50°C. The goal of our development is to build a similar CPC based on the TSI 3010 model with a new and independent heating and cooling system. This allows more flexibility to adjust temperatures and flow rate. The original flow control with a critical orifice and a heavy pump is replaced by a laminar flowmeter and a miniature rotary vane pump. The saturator temperature (Ts), the condenser temperature (Tc) and the flow rate of the instrument are totally controlled by the user.

CALIBRATION

The detection efficiency is measured with an aerosol electrometer (Faraday cage + Keithley electrometer) with standards sub 2 nm ions produced with electrospray classified by a high resolution DMA (Attoui
type) for different temperature differences (ΔT = Ts - Tc) and flowrates. Careful attention has been paid in selecting the thermoelectric coolers (Peltier elements) and designing their power supply, in order to achieve a lower saturator temperature than in most commercial CPCs (typically 10°C). Low condenser temperature helps to keep a high ΔT at relatively low saturator temperature in order to decrease evaporation losses of volatile particles and thermal diffusion losses in the saturator. The saturator and condenser are thoroughly insulated to minimize heat losses, and hence, power consumption. The CPC is designed to be powered by a 28VDC power source, making the instrument lighter and easier to integrate in research aircrafts.

Detection efficiency were characterized with hydrophobic particles produced by evaporation-condensation of ammonium sulfate with an oven, as well as with singly charged positive and negative, hydrophobic particles of tungsten oxides and nickel chromium oxides, produced by a hot wire generator, down to 1 nm.

Figure 1. Counting efficiency of boosted CPC and stock TSI 3010.

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REFERENCES


ELECTROSPRAY GENERATION OF SIGNLY CHARGED SUB-4 NM CLUSTERS

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Keywords: ELECTROSPRAY, CLUSTER, PARTICLE GENERATION

INTRODUCTION

Electrospray (ES) production of charged clusters has been utilized in aerosol science to study for example evaporation and cluster collision cross sections, since the produced clusters are well defined in terms of structure, chemical properties, electrical mobility and so on. Another common application for the electrospayed clusters is characterization of instruments which are specialized for sub-5 nm particle measurement. These experiments include for example differential mobility analyzer (DMA) sheath flow rate calibration or measurement of condensation particle counter (CPC) detection efficiency. In instrument characterization experiments, the ES produced clusters have been used mostly in sizes below 2 nm in mobility diameter. This is due to that the ES produces also multiply charged liquid droplets and large sample residues, of which electrical mobility diameter are in the range of 2 nm and larger (Ude and Fernández de la Mora, 2005). Separation of these multiply charged species from the singly charged ones requires tandem high resolution DMA technique (Attoui et al., 2013), which has two immediate downsides: not many laboratories possess the tandem high resolution DMA technology, and cluster concentrations downstream of the second DMA can be low due to relatively weak DMA particle transmission efficiency. Neutralization of electrospayed droplets via diffusion charging is a well-known method for production of singly charged aerosol (Chen et al., 1995), but has not been shown in the size range of 2 to 5 nm with high resolution DMA techniques able to resolve the individual clusters. In this study we show that generation of super-2 nm electrospayed clusters by neutralizing the multiply charged droplets, allowing the super-2 nm clusters to be studied with a single DMA.

METHODS

The experimental setup used in this study is presented in Figure 1. The difference to the commonly used setup is that the ES produced droplets are neutralized, and between the neutralizer and the DMA a copper tube of 60 cm in length and 4 mm in inner diameter was placed. This was to increase the residence time upstream of the DMA and allow more complete neutralization to take place. Tetradodecylammonium bromide (TDDABr) clusters were produced with the ES and size selected with a Herrmann type high resolution DMA (Kangasluoma et al., 2016). Neutralization was studied by measuring the ratio (PSM/AEM) of the concentration detected by a mixing type CPC (PSM) to the concentration detected by an aerosol electrometer (AEM). If neutralization is incomplete, PSM/AEM is low, since PSM counts highly charged droplets as single particle while AEM counts them according to charge. The ES carrier flow rate was varied between 6 and 15 liter per minute (lpm) to vary the neutralization time of the clusters, and study PSM/AEM.
Figure 1. The experimental setup. 60 cm long tube was inserted between the neutralizer and DMA to allow more time for neutralization.

RESULTS

Figure 2 presents the PSM/AEM ratio for particles of 4 nm in mobility diameter with different residence times downstream of the neutralizer. At residence times larger than approximately 0.06 s the PSM/AEM ratio saturates, suggesting complete neutralization of the produced clusters. This helps significantly in using ES produced clusters in studying CPC detection efficiency, as now the upper size limit of 2 nm due to multiply charged particles is pushed to at least up to 4 nm, which is enough to characterize CPCs specialized for sub-3 nm particle detection.

Figure 3 presents mobility spectrum of neutralized TDDABr. Clusters are resolved up to nonamer in negative polarity, corresponding to 3.8 nm in mobility diameter. More careful study of the peak width suggests their widening with increasing size more than would be expected from the DMA sizing resolution. This widening suggests impurities in the clusters, which can originate from the radioactive source or from the sample or solvent material. This is under further research.

Figure 2. PSM/AEM ratio as a function of the neutralization time. Saturation of the curve suggests complete neutralization of the particles.
CONCLUSIONS

We have shown production of monomobile, or at least quasi-monomobile, and singly charged clusters by neutralizing and mobility classifying clusters from ES source. The fact that the clusters are singly charged makes it possible to use the clusters in characterizing sub-3 nm CPCs. More characterization experiments will be conducted to verify the exact chemical composition of the clusters, and the effects possibly altering the composition from the pure (AB)A+ or (AB)B- ion pair structure.

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IMPROVED COUNTING STATISTICS OF AN ULTRAFINE DMPS SYSTEM BY UTILIZING ULTRAFINE A20 CPC WITH OPTICS FLOW RATE OF 2.5 LPM

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INTRODUCTION

A Differential Mobility Particle Sizer (DMPS) system can be used to measure ambient aerosol number size distribution (e.g. Wiedensohler et al., 2012). DMPS system is a combination of a charger to give particles an electric charge, Differential Mobility Analyzer (DMA) for size classification of the particles, and a Condensation Particle Counter (CPC) to measure the number concentration of these size-selected particles (Aalto et al., 2001). In this study, we compare the counting statistics of a modified Airmodus A20 CPC and a TSI 3025 CPC utilized in a DMPS system.

METHODS

The TSI 3025 is a continuous-flow CPC (Stolzenburg and McMurry, 1991). In the 3025, the aerosol sample is saturated by passing it over a heated pool of liquid n-butanol. In the condenser tube the air is cooled by thermal diffusion, this causes the butanol to condense onto the particles. The grown particles pass through a lighted viewing volume where they scatter light in pulses as they pass through. The scattered-light pulses are detected by a photodetector and converted into electrical pulses. The particle concentration is given by the calculated rate of these electrical pulses. The sample flow through the 3025 optics is 0.03 liters per minute (lpm).

The Airmodus A20 CPC is a laminar-type CPC (Kangasluoma et al., 2015). In the A20 the entire aerosol sample is heated and saturated with butanol vapor. The saturated flow then goes through a multitube condenser (6 tubes) where the flow is cooled down causing the butanol to condense onto the particles. The sample flow through the optics in the A20 is increased 2.5 lpm. Conventional unsheathed CPCs can be tuned for even sub-3 nm particle detection by increasing the temperature difference of the saturator and condenser, and adjusting the inlet flow rate. (Kangasluoma et al., 2015). In this study the A20 flow rate was increased to 2.5 lpm to decrease diffusional losses of the smallest particles and to further increase the counting statistics. Because the optics flow rate of the A20 is 50 times greater than that of the 3025, we expect to see smaller uncertainties for the A20 compared to the 3025.

RESULTS

Calibration of the CPCs is done using a tube furnace as an aerosol source. After the furnace is a dilution system is used to keep the concentrations low enough to avoid coincidence in the CPC optics. A radioactive source gives the particles an electric charge before they go to the DMA. The size-selected particles are then divided to A20, 3025, and an electrometer (EM). The EM is used as a reference for the calibration. The cut-off calibrations for both CPCs are presented in the figure 1. Detection efficiency for the 3 nm particles is about 20% for the modified A20 and 60% for the 3025.

A20 and 3025 CPCs were used in parallel as counters of a DMPS system at Station for Measuring Ecosystem-Atmosphere Relation (SMEAR III, Järvi et al. 2009) in Helsinki, Finland. Total counts detected by the CPCs during the specified counting time as a function of particle diameter for both CPCs are presented in the figure 2. In our system, the counting time changes as a function of the particle diameter in order to improve the system performance particularly for the smallest aerosol particles. The results show that the total counts detected during the counting time by the A20 are higher...
than those of the 3025 within the whole measurement range of 3-40 nm. Uncertainties related to counting
statistics can be expressed as \( \sqrt{N/N} \), where \( N \) is the number of counts. Using this knowledge, in figure 3
illustrates the calculated uncertainties for the A20 and 3025 CPCs as a function of particle diameter
obtained from the means of the total counts seen by the CPCs (figure 2).

Figure 1. Detection efficiencies of the modified Airmodus A20 and TSI 3025 CPCs as function of particle
mobility equivalent diameter

Figure 2. Comparison of total counts seen by A20 and 3025 CPCs as a function of particle size.
CONCLUSIONS

From the results presented in this study, we see that we do get improved counting statistics of an ultrafine DMPS system by utilizing a modified A20 CPC with optics flow rate of 2.5 liters per minute. The total counts measured by the A20 are higher than those measured by the 3025, when used parallel in a DMPS system. From the same data, we also see that the uncertainty related to the counting statistics is smaller for the modified A20 due to increased flow rate. The improved counting statistics of the CPC, allows one to increase the size resolution of the DMPS system.

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