

REPORT SERIES IN AEROSOL SCIENCE

N:o 159 (2014)

CONTRIBUTION OF BIOGENIC VOLATILE ORGANIC
COMPOUNDS TO THE FORMATION AND GROWTH OF
PARTICLES IN THE ATMOSPHERE - FROM MOLECULE
CLUSTER TO CLOUD CONDENSATION NUCLEI

LI LIAO

Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation

*To be presented, with the permission of the Faculty of Science
of the University of Helsinki, for public criticism in auditorium E204,
Gustaf Hällströmin katu 2, on December 16th, 2014, at 2 p.m.*

Helsinki 2014

Author's Address: Department of Physics
P.O. Box 64
FI-00014 University of Helsinki
li.liao@helsinki.fi

Supervisors: Professor Markku Kulmala, Ph.D.
Department of Physics
University of Helsinki

Associate Professor Miikka Dal Maso, Ph.D.
Department of Physics
Tampere University of Technology

Docent Michael Boy, Ph.D.
Department of Physics
University of Helsinki

Reviewers: Docent Lauri Laakso, Ph.D.
Finnish Meteorological Institute, Marine Research

Docent Aki Virkkula, Ph.D.
Finnish Meteorological Institute, Air Quality Research

Opponent: Associate Professor Annele Virtanen, Ph.D.
Department of Applied Physics
University of Eastern Finland

ISBN 978-952-7091-06-7 (printed version)

ISSN 0784-3496

Helsinki 2014

Unigrafia Oy

ISBN 978-952-7091-07-4 (pdf version)

<http://ethesis.helsinki.fi>

Helsinki 2014

Helsingin yliopiston verkkojulkaisut

Acknowledgements

The research presented in this thesis was carried out in the Department of Physics, University of Helsinki. I express my gratitude to the former and present head of the department, Prof. Juhani Keinoen and Prof. Hannu Koskinen for providing me the working facilities.

I thank Prof. Markku Kulmala for giving me the opportunity to work at the Division of Atmospheric Sciences, and for providing the tools and work environments that supported me to pursue my Ph.D. I am grateful to Assoc. Prof. Miikka dal Maso and Doc. Michael Boy for supervising my research work and for countless discussions related to various sciences or life matters. I am thankful to Prof. Veli-Matti Kerminen for many thoughtful scientific comments and discussions. Doc. Lauri Laakso and Doc. Aki Virkkula are gratefully acknowledged for carefully reviewing this thesis.

This work would not have been possible to complete without the helps and supports of my colleagues. I am greatly thankful to all my co-authors and to everyone I have had interesting and inspiring discussions. Especially, I want to thank Ditte Mogensen, Putian Zhou, Pontus Roldin, Janne Korhonen, Tuomo Nieminen, Henri Vuollekoski, Anna Nikandrova and Stephany Mazon.

I thank the Maj and Tor Nessling Foundation for partially funding the work carried for this thesis.

I am thankful to all my friends in Finland for helping me get through the difficult times and for all the emotional supports, entertainments and caring you provided. I am grateful to my family for always supporting me with their unconditional love. Finally, I deeply thank Reinis Švarcbahs for the love and companionship.

Li Liao

University of Helsinki, 2014

Abstract

Atmospheric aerosol particles influence the Earth's climate system, affect air visibility, and harm human health. Aerosol particles originate from both anthropogenic and biogenic sources, either from direct emissions or secondary particle formation. Secondary particle formation from gas phase precursors constitutes the largest fraction of global aerosol budget, yet large uncertainties remain in its mechanisms. This thesis attempted to study the source, the formation mechanisms, and the sink of secondary particles based on data analysis of field measurements and chamber experiments. In addition, numerical simulations were performed to model the processes of secondary particle formation observed in the chamber experiments.

We summarized our findings into five main conclusions: 1) Monoterpenes originated from anthropogenic sources (e.g. forest industry) can significantly elevate the local average concentrations and result in a corresponding increase in local aerosol loading; 2) Monoterpenes from biogenic emissions show direct link to secondary particle production: the secondary aerosol masses correlate well with the accumulated monoterpene emissions; 3) Temperature influences biogenic monoterpene emissions, resulting in an indirect effect on the biogenic secondary particle production and corresponding cloud condensation nuclei (CCN) formation; 4) Both data analysis and numerical simulation suggested that nucleation involving the oxidation products of biogenic volatile organic compounds (VOCs) and H_2SO_4 better explains the nucleation mechanism, yet the specific VOCs participating in the nucleation process remains uncertain; 5) The numerical simulation showed evidence of vapor wall loss effect on the yield of secondary particles from the chamber experiments; a reversible gas-wall partitioning had to be considered to properly capture the observed temporal evolution of particle number size distribution during the chamber experiments.

The results of this thesis contribute to the understanding on the role of monoterpenes to secondary particle formation. This thesis raises caution on the parameterization of the temperature dependence of biogenic secondary particle formation in predicting the aerosol production potential due to rising temperatures in the future. This work also points out a way for improving the comprehensive numerical models to better understand the secondary particle formation processes and related climatic effects.

Keywords: BVOC emission, monoterpenes, new particle formation, temperature, SOA

Contents

1	Introduction	7
2	Atmospheric new particle formation	11
2.1	Gas precursors of the secondary particles	11
2.1.1	Inorganic gases	13
2.1.2	Terpenoids	14
2.2	Aerosol dynamics	15
2.2.1	Cloud condensation nuclei activation	17
3	Measurement and methods	19
3.1	Atmospheric field measurements	19
3.1.1	Instruments	20
3.1.2	Backward trajectories	22
3.2	Jülich Plant Atmosphere Chamber	22
3.3	MALTE-BOX model (Atmospheric simulation/modeling)	24
4	Results and discussions	27
4.1	Connection between monoterpenes and aerosol particles from anthropogenic origin	27
4.2	Linking the biogenic monoterpene emissions and natural aerosol production	28
4.3	Temperature response of the natural aerosol production potential	30
4.4	Simulation of the new particle formation from tree emissions in JPAC chamber	31
5	Review of papers and the author's contribution	35
6	Conclusions	37
	References	40

List of publications

This thesis consists of an introductory review, followed by 5 research articles. In the introductory part, these papers are cited according to their roman numerals. **Paper I** is reproduced with the permission from the Boreal Environment Research Publishing Board. **Paper II–V** are reproduced under the Creative Commons Attribution License.

- I** Liao, L., Dal Maso, M., Taipale, R., Rinne, J., Ehn, M., Junninen, H., Äijälä, M., Nieminen, T., Alekseychik, P., Hulkkonen, M., Worsnop, D. R., Kerminen, V.-M., and Kulmala, M. (2011). Monoterpene pollution episodes in a forest environment: indication of anthropogenic origin and association with aerosol particles, *Boreal Env. Res.*, 16:288–303.
- II** Sihto, S.-L., Mikkilä, J., Vanhanen, J., Ehn, M., Liao, L., Lehtipalo, K., Aalto, P. P., Duplissy, J., Petäjä, T., Kerminen, V.-M., Boy, M., and Kulmala, M. (2011). Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest, *Atmos. Chem. Phys.*, 11:13269–13285.
- III** Liao, L., Kerminen, V.-M., Boy, M., Kulmala, M., and Dal Maso, M. (2014). Temperature influence on the natural aerosol budget over boreal forests, *Atmos. Chem. Phys.*, 14:8295–8308.
- IV** Liao, L., Dal Maso, M., Mogensen, D., Roldin, P., Rusanen, A., Kerminen, V.-M., Mentel, T. F., Wildt, J., Kleist, E., Kiendler-Scharr, A., Tillmann, R., Ehn, M., Kulmala, M., and Boy, M. (2014). Modelling the Contribution of Biogenic VOCs to New Particle Formation in the Jülich Plant Atmosphere Chamber, *Atmos. Chem. Phys. Discuss.*, 14:27973–28018.
- V** Dal Maso, M., Liao, L., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Sipilä, M., Hakala, J., Lehtipalo, K., Ehn, M., Kerminen, V.-M., Kulmala, M., Worsnop, D., and Mentel, T. F. (2014). A chamber study of the influence of boreal BVOC emissions and sulphuric acid on nanoparticle formation rates at ambient concentrations, *Atmos. Chem. Phys. Discuss.*, Accepted.

1 Introduction

“ 回头下望人寰处， 不见长安见尘雾。 ”

— 白居易

Over a thousand years ago, Bai Juyi, one of the most famous Chinese poets from the Tang Dynasty, wrote a poem called ‘cháng hèn gē’. In the poem, it was written that “Looking back far from the residential area, you no longer see the city, but only the dust and haze (translated from the Chinese above)”. The research of this thesis dealt with even smaller particles than the dust the poet had seen. Indeed, the atmosphere covering the Earth consists of not only gas molecules, but also particles that human eyes cannot always see. An aerosol is defined as a suspension of solid or liquid particles in a gas (Seinfeld and Pandis, 2012). The size range of aerosol particle diameters spans five orders of magnitude from approximately one nanometer (nm) up to hundreds of micrometers (μm). Aerosol particles are generally discussed in terms of their number or mass concentration and size distribution, depending on their origins or the techniques used to measure them. This thesis mostly dealt with the particle number concentration and corresponding size distribution of submicrometer particles. The number concentration of aerosol particles, being many orders of magnitude lower than the atmospheric gas concentration, ranges from several particles per cm^3 in clean air in Antarctica (Järvinen et al., 2013; Kyrö et al., 2013) to up to hundreds of thousands of particles per cm^3 (Shen et al., 2011; O’Dowd et al., 2002). The smallest aerosol clusters can be formed from the collision and stabilization of the gas molecules in atmosphere (Kulmala et al., 2007, 2013a, 2014b). This process is called atmospheric nucleation, and was one of the main research focuses in this thesis.

Atmospheric aerosol particles influence the Earth’s climate system on regional and global scale, through several mechanisms. First, aerosol particles can directly absorb and scatter the solar radiation. Second, aerosol particles can absorb, scatter, and emit thermal radiation (Haywood and Boucher, 2000; Carslaw et al., 2010). Third, aerosol particles can act as cloud condensation nuclei (CCN) which alter the formation, precipitation efficiency, and the optical properties of clouds (Anderson et al., 2003; Stier et al., 2007; Andreae and Rosenfeld, 2008; Kerminen et al., 2012). Overall, the

radiative forcing caused by aerosol particles and their interactions with clouds is the largest source of uncertainty which limits the understanding of past and future climate changes (IPCC 2013, Fig. 1). Thus it is encouraging to carry out intensive studies on aerosols, in order to narrow down the scientific uncertainties and to better understand the past, current, and future climate changes.

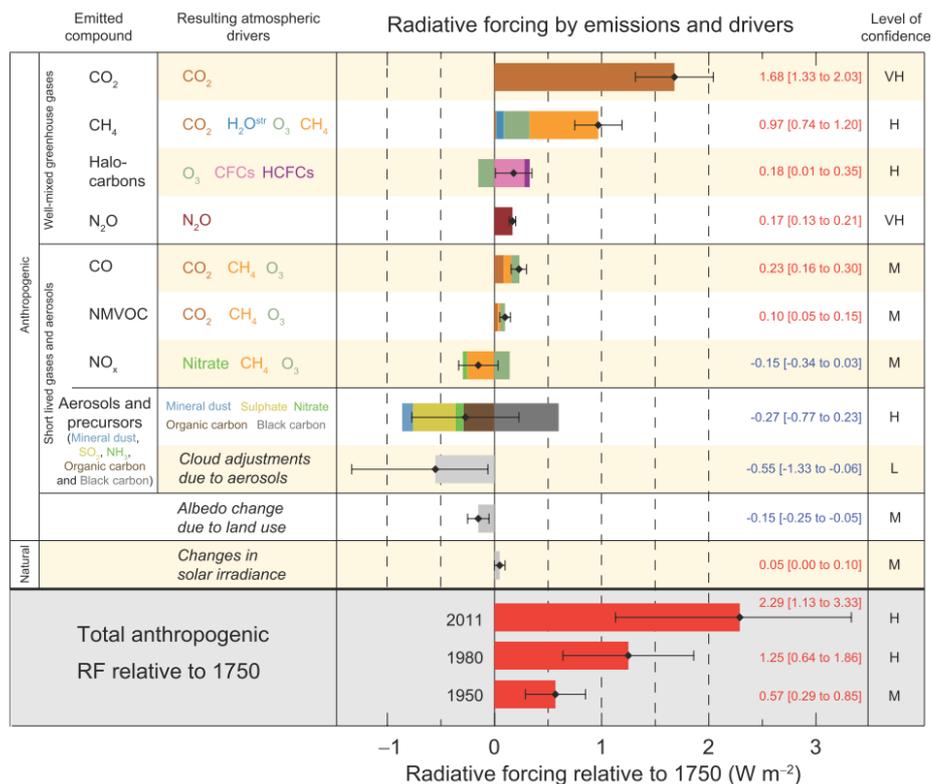


Figure 1: Radiative forcing estimates in 2011 relative to 1750 and aggregated uncertainties for the main drivers of climate change. Values are global average radiative forcing, partitioned according to the emitted compounds or processes that result from a combination of drivers. Total anthropogenic radiative forcing is provided for three different years relative to 1750 (Reproduced from IPCC, 2013).

From the local to regional scale, aerosol particles may decrease air visibility and impact air quality. Also, aerosol particles may be harmful to human health (Douwes et al., 2003). These two effects are usually linked, especially in heavily polluted urban cities where high levels of particulate matters (PM) are present (PM_{2.5} and PM₁₀ are particles less than 2.5 or 10 μm in diameter respectively). The low air visibility is primarily

caused by the high mass burden of $\text{PM}_{2.5}$ (Han et al., 2013). Many epidemiological studies have shown the association between the PM exposures and the cardiovascular and respiratory diseases (Sun et al., 2010, and references therein). The elevation of the fine PM has also been associated with an increased risk of mortality (Pope et al., 2004).

The sources of aerosol particles include primary emission (such as mineral dust, pollen, soot etc.) and secondary particle formation from both anthropogenic and natural origins. The new particle formation events, i.e. aerosol particles formed from homogeneous nucleation and condensational growth with gas precursors, present an important source of the tropospheric aerosol particle number concentration (Kulmala et al., 2004b, and references therein). The processes explaining the observed new particle formation events are one of the greatest unsolved questions in aerosol science. This is, firstly because several instruments, e.g. Particle Size Magnifier (PSM), Neutral cluster and Air Ion Spectrometer (NAIS), Balance Scanning Mobility Analyzer (BSMA), and Atmospheric Pressure Interface Time-Of-Flight mass spectrometer (APi-TOF), are able to directly measure freshly formed aerosol clusters and their precursors; and secondly because of the complex gas-phase chemistry with millions of different species, especially from the biogenic emissions.

Secondary organic aerosol (SOA) formed from biogenic volatile organic compounds (BVOCs) accounts for the most significant part of the global aerosol particle mass budget (Spracklen et al., 2011; Hallquist et al., 2009). SOA formation has been shown to increase the regional CCN concentrations (Kerminen et al., 2012). Therefore, the field of SOA and its anthropogenic and biogenic precursors connect the ‘vegetation, aerosols, and climate system’ (Andreae and Crutzen, 1997; Kulmala et al., 2004a; Kanakidou et al., 2005; Kulmala et al., 2013b, 2014a). The boreal forest-emitted terpenes (one class of BVOCs) has been shown a direct link to the SOA production (Tunved et al., 2006; Cahill et al., 2006, **Paper III**). Biogenic terpene emissions are strongly temperature dependent and dominate the total BVOC emission budget globally (Guenther et al., 1995; Oderbolz et al., 2013). Therefore, with temperature projected by IPCC (2013) to rise in the future, the change of the vegetation patterns may cause an even stronger aerosol effect via changing the BVOC emission patterns (Paasonen et al., 2013). On the other hand, the uncertainty of the SOA loading may prompt bigger errors on the projection of the future temperatures (Stevens, 2013; Andreae et al., 2005).

Two hypotheses are the main focus of this study:

(1) The reactivity of various VOC species from both biogenic emissions and anthropogenic origins, and the relative quantity of different species in the emitted BVOC mixtures have a strong effect both on the particle number concentration and the SOA mass formation.

(2) Changes in the BVOC emissions in response to different environmental conditions (e.g. temperature) lead to changes in the aerosol production potential, which result in changes in the CCN numbers and eventually in the radiative balance.

These hypotheses will be tested using field measurements, chamber experiments, and a numerical model, via detailed analysis of the most relevant parameters and processes in the ‘vegetation-aerosol-climate’ system. The main objectives in this thesis thus include,

- To quantify the anthropogenic source of monoterpenes and its connection with aerosol particles in a boreal forest environment;
- To determine the linkage between biogenic monoterpene emissions and SOA mass production during air mass transport over Nordic boreal forest region;
- To investigate the temperature influence on the connection between biogenic monoterpene emissions, SOA and CCN production;
- To evaluate the contribution of BVOC emissions to the formation mechanisms of secondary particles from chamber experiments;
- To examine the influence of vapor wall losses on the SOA yield in a simulation chamber.

We will discuss these research questions in the introductory part together with the five articles included in this thesis.

2 Atmospheric new particle formation

Atmospheric new particle formation describes the formation and growth of secondary particles from gas precursors via gas-to-particle conversion. New particle formation events have been observed globally both in the planetary boundary layer and the free troposphere (Covert et al., 1992; Hoppel et al., 1994; Kulmala et al., 2004b; Kulmala and Kerminen, 2008). The traditional interpretation of the new particle formation process includes three steps: firstly atmospheric chemical oxidation of gas compounds forming low volatility gas precursors, secondly, the formation of nano-clusters from the gas precursors (homogeneous nucleation), and thirdly condensational growth of the formed particles. In addition, Kulmala et al. (2014b) improved this traditional gas-to-particle conversion scheme in a more detailed five-step process, in which the gas precursors were classified into several groups for different steps. Specially, the extremely low-volatile products were introduced in this scheme.

Fig. 2 depicts a typical new particle formation event observed from 3 to 1000 nm particle number size distributions measured by a DMPS (Differential Mobility Particle Sizer) system on 10 April 2014 at the SMEAR II station, Hyytiälä, Finland. One can see that the smallest (3 nm) aerosol particles were substantially formed around noon on the first day, and continued to grow to larger sizes (about 100 nm) till around noon on the second day (Case I). In this section, we will introduce both the aerosol gas precursors and the basic processes which govern the secondary aerosol particle formation.

In addition, one could clearly distinguish two strong elevations of the aerosol particle numbers (Case II) before the occurrence of the new particle formation event in Fig. 2. This elevation of aerosol particle numbers co-occurred with an increase in the monoterpene concentrations (see the top panel in Fig. 2), which drew our interest, and we investigated the particular phenomenon in **Paper I**.

2.1 Gas precursors of the secondary particles

Atmospheric gas compounds which contribute to the formation and growth of the secondary aerosol particles are named aerosol gas precursors. In addition, atmospheric ions may also contribute to the aerosol nucleation processes (Hamill et al., 1982; Raes

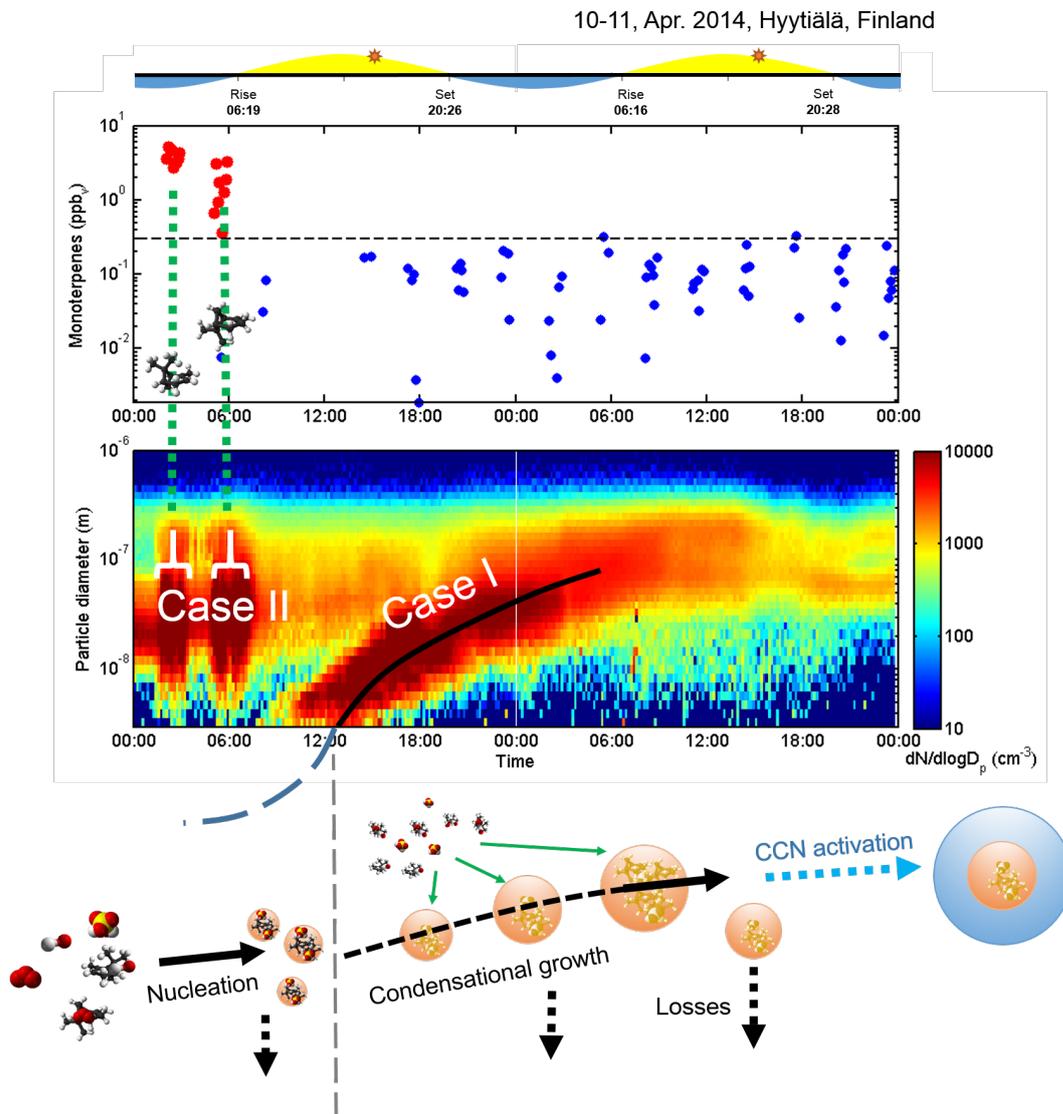


Figure 2: An example case (Case I) of a new particle formation event observed on 10 April 2014 at the SMEAR II station, Hyytiälä, Finland, together with a schematic picture depicting the main aerosol dynamic processes from nucleation to CCN activation. In addition, an example case (Case II) of the observed aerosol particle elevation from anthropogenic origins together with the increased monoterpene concentrations (red dots). The blue markers are monoterpene concentrations. The sunrise and sunset time on these two days are illustrated on the topmost panel.

et al., 1986; Hirsikko et al., 2011; Yu and Turco, 2000). In general, these gas compounds should either have very low volatility (e.g. low volatile VOCs) or be able to facilitate the formation of low-volatile complexes (e.g. H_2SO_4 , water, amines, ammonia), in order to participate in the gas-particle conversion processes (Eisele and Tanner, 1990; Hoppel et al., 1994; Kulmala et al., 2014b). In the atmosphere, low volatility compounds are usually products from VOC oxidation with OH, O_3 and NO_3 .

2.1.1 Inorganic gases

H_2SO_4 has been shown as an important compound explaining the secondary particle formation. H_2SO_4 is usually formed via OH oxidation of SO_2 in air. The source of SO_2 includes both anthropogenic origins (e.g. industrial processes and combustion) and natural emissions (e.g. volcanic eruptions (Wallace, 2001), and dimethyl sulfide (DMS) from marine phytoplankton (Ayers et al., 1997)). SO_2 has been recognized as an air pollutant for decades, mainly because of the formation of acid rain. Thus substantial reduction on SO_2 emission has been made via governmental regulations. For example, the emission of SO_2 in Europe has decreased by 74 % between 1990 and 2011 (EEA, 2014). However, some studies suggested that such pollutant control may accelerate the climate changes, because of reduction of short-lived pollutants (especially sulfate aerosols) with negative forcing (Arneth et al., 2009).

Atmospheric H_2SO_4 concentrations can be measured by CIMS (Chemical Ionization Mass Spectrometer) (Petäjä et al., 2009, **Paper V**). The measured H_2SO_4 concentrations vary between the locations, and the average ambient H_2SO_4 concentration in continental environments is about 10^6 – 10^7 molecules cm^{-3} (Petäjä et al., 2009; Zheng et al., 2011). In addition to OH oxidation, reactions of stabilized Criegee intermediate (sCI) with SO_2 could also contribute to H_2SO_4 (Mauldin III et al., 2012; Boy et al., 2013). Many studies have shown that H_2SO_4 is closely linked to the new particle formation with a consistent correlation between the H_2SO_4 concentration and the new particle formation rate (Sipilä et al., 2010; Sihto et al., 2006; Riipinen et al., 2007; Kulmala et al., 2000). This empirical parameterization of H_2SO_4 to explain the nucleation mechanism will be discussed in the aerosol dynamics section.

Ammonia and amines have been found in the composition of aerosol particles, whereas the air chemistry leading to the secondary particle formation from reactions of gaseous ammonia or amines remains uncertain (Eisele and Tanner, 1990; Murphy

et al., 2007). Kulmala et al. (2013a) suggested a potential path of ammonia or amines participating in the initial steps of nucleation. Ammonia has been found to enhance the nucleation rate by 2–3 orders of magnitude (Kirkby et al., 2011), and amines can enhance particle formation rates more than 3 orders of magnitude compared with ammonia (Almeida et al., 2013).

2.1.2 Terpenoids

Terpenoids are the most abundant biogenic VOCs accounting for more than half of the global BVOC emission (Guenther et al., 2012; Oderbolz et al., 2013). Terpenoids include compounds consisting of one to several isoprene units, e.g. isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$). Due to the level of relevant importance in SOA formation, the focus of this work is on monoterpenes and their SOA production potential.

Biogenic origin of terpenes dominates the total emission budget globally (Guenther et al., 1995). Biogenic monoterpene emission is strongly temperature and light dependent, with seasonal and diurnal variations (Tarvainen et al., 2005), whereas some studies suggested that a temperature dependent emission algorithm can well describe the biogenic monoterpene emission (Bertin et al., 1997; Tarvainen et al., 2005). We used a simplified monoterpene emission algorithm to estimate the accumulated biogenic monoterpene concentrations from the back trajectory study in **Paper III**. The total flux of monoterpenes was derived from the following equation (Steinbrecher et al., 1999):

$$F = \varepsilon D \gamma \quad (1)$$

where F ($\mu\text{g m}^{-2} \text{h}^{-1}$) is the total flux of monoterpenes from the boreal forest, ε is the standard emission potential for the coniferous species ($1.5 \mu\text{g g (dry weight)}^{-1} \text{h}^{-1}$), and D is the foliar biomass density. γ is the environmental correction factor of temperature dependence on monoterpene emission rates, calculated from $\gamma = \exp(\beta(T - T_s))$ where $\beta = 0.09 \text{ }^\circ\text{C}^{-1}$, and $T_s = 303.15 \text{ K}$.

Anthropogenic origin of terpenes due to human activities may also significantly contribute to the local or regional VOC budgets. Studies have shown that a large amount of VOC compounds are emitted from wood processing in forestry and the forest industry, during the processes of machining, logging, chipping, drying, debarking, sawing and pulping (Schade and Goldstein, 2003). The drying process dominates the

VOC emissions from the sawmill industry, in which terpenes account for the major part among the total emitted VOC compounds (Englund and Nussbaum, 2000). In **Paper I**, we examined the anthropogenic source of monoterpenes measured at one field station, and quantified the average anthropogenic contribution to the local monoterpene concentrations.

BVOC oxidation produces extremely low volatile organic compounds (ELVOCs) essential to the new particle formation process (Ehn et al., 2014; Kulmala et al., 2014b), and BVOC oxidation products constitute the largest source of SOA, accounting for the main composition of SOA condensational growth (VanReken et al., 2006; Hao et al., 2011; Riipinen et al., 2012). Monoterpene oxidation products have shown substantial contribution to SOA formation (Laaksonen et al., 2008). The ozonolysis of sesquiterpenes may also initiate new particle formation (Bonn and Moortgat, 2003). Isoprene oxidation has been linked to SOA formation (Surratt et al., 2006), whereas high reactivity of isoprene with OH may suppress new particle formation process (Kiendler-Scharr et al., 2009). Nevertheless, the exact contribution of BVOCs to the new particle formation process still remains uncertain, especially in the first steps of nucleation.

2.2 Aerosol dynamics

Homogeneous nucleation is the initial steps of atmospheric new particle formation. Previous studies have found that the observed new particle formation rates show good correlation with the measured H_2SO_4 concentrations to the power of 1 or 2 (Riipinen et al., 2007; Weber et al., 1996; Paasonen et al., 2010, **Paper IV**), although this correlation cannot fully explain all the observed features of this process (Boy et al., 2003). Nevertheless, these correlations are the empirical parameterizations which are most frequently used when modeling new particle formation. The proposed mechanisms are modeled with following equations (Kulmala et al., 2006):

$$J = K \times [\text{H}_2\text{SO}_4], \quad (2)$$

or

$$J = K \times [\text{H}_2\text{SO}_4]^2, \quad (3)$$

where J is the atmospheric nucleation rate ($\text{cm}^{-3} \text{s}^{-1}$), A is the activation coefficient. K is termed as ‘kinetic nucleation coefficient’, including both the collision frequency and the probability of formation of a stable particle after the collision (Paasonen et al., 2010)

and $[\text{H}_2\text{SO}_4]$ is the sulfuric acid concentration. We tested the kinetic H_2SO_4 nucleation mechanism using the Jülich Plant Atmosphere Chamber (JPAC) experiments in **Paper IV**.

Nucleation involving both organic oxidation products and H_2SO_4 has also been suggested as a potentially important mechanism, assuming that both H_2SO_4 and VOC oxidation products can activate the clusters (Paasonen et al., 2010; Riccobono et al., 2014). In this study, the organic nucleation is modeled with the following equation:

$$J = P \times [\text{H}_2\text{SO}_4] \times [\text{VOCs}], \quad (4)$$

where P is coefficient for the organic nucleation (Paasonen et al., 2010). In **Paper IV**, we tested the use of ELVOCs as the organic precursors involved in the formation (Eq. 4) and growth of new particles in the JPAC chamber.

Condensation is the gas-to-particle transfer of gases onto existing aerosol particles. Condensation is the main process explaining the growth of atmospheric particles, and it alters the chemical compositions and changes the size distributions of aerosol particle populations. Condensation is well understood in terms of the basic mechanisms, the mass flux of the gas vapor i to the particle phase is determined by (Seinfeld and Pandis, 2012):

$$\frac{dm}{dt} = \frac{2\pi M_i (d_p + d_i) (D_p + D_i) \beta_m (p_i - p_{eq,i})}{RT} \quad (5)$$

where M_i is the molecular weight, D_p and D_i are diffusion coefficients for the particle and for the gas compound i in air. d_p and d_i are the diameters of the particle and gas i . β_m is the Fuchs-Sutugin transition-regime correction factor. The difference between the gas vapor i far from the particle p_i and the equilibrium vapor pressure $p_{eq,i}$ at the particle surface determines the condensational growth rate due to the vapor i . This happens only when the partial pressure of the gas compound p_i is higher than the vapor pressure at the particle surface. Otherwise, *evaporation* of the gas compounds occurs from particle phase back to gas phase.

However, information on the properties of the condensing vapors (e.g. their saturation vapor pressures) is very limited (Topping et al., 2007), which may cause challenge to determine the particle condensational growth from e.g. the mixtures of biogenic emissions. In **paper IV**, we used a simplified model with condensable compounds lumped into two volatility classes (ELVOCs and SVOCs (semi-volatile organic compounds)).

Coagulation refers to the process when two particles collide, stick together and form a larger particle. This reduces the total particle number concentrations while keeping the particle mass concentration intact. Coagulation mostly happens between particles with large size difference, as the large particles provide big surface area for the small particles having high diffusion velocity. Therefore, coagulation is often the main sink process for the freshly formed nucleation-mode particles.

Deposition is the mechanism of atmospheric particle removal from air, including both wet and dry depositions. Wet deposition describes particles removed by in-clouds scavenging or by precipitation (e.g. rain, snow). Dry deposition is the other particle loss process without the influence of clouds and precipitation. The dry deposition depends mostly on the sizes of particles and the surface structures. In this thesis, we adapted a simplified deposition mechanism to calculate the particle loss along air mass transport, in which the aerosol particle loss as a function of particle size was derived from the discrete deposition equation (**Paper III**),

$$\frac{dN_{i,loss}(t)}{dt} = \gamma N_i(t) \quad (6)$$

where γ is the size-dependent particle deposition rate (h^{-1}), $dN_{i,loss}$ is the number of deposited particles at size bin Dp_i , and dt is the time derivative. This approach takes into account particle dry deposition inside the boundary layer, including their impaction and diffusion losses on the surfaces.

In addition, one should pay special attention to the wall depositions of both aerosol particles and gas compounds in the chamber experiments (**Paper IV**). The calculation of chamber wall losses is discussed in Section 3.3.

2.2.1 Cloud condensation nuclei activation

Secondary particles formed from gas precursors can act as the seeds of cloud droplets or cloud ice particles, when particles are larger than the critical diameters for supersaturated water vapor condensing on them. These particles are named cloud condensation nuclei (CCN). CCN are critical for the cloud formation, as water vapor cannot form droplets homogeneously in the atmosphere, thus each cloud droplet is formed from at least one aerosol particle. The critical diameter for aerosol particles to be activated as CCN is generally in the size range of 50–100 nm (Kerminen et al., 2012), depending

on the surrounding vapor pressure and hygroscopic properties of the particles (Virkkula et al., 1999). The water uptake by the aerosol particles can be described by the Köhler equation (Köhler, 1936):

$$S = a_w \exp\left(\frac{4M_w\sigma}{RT\rho d_{wet}}\right) \quad (7)$$

where S is the water saturation ratio, a_w is the water activity, M_w is the molar mass of water, σ is the surface tension of the solution, R is the universal gas constant, T is temperature, ρ is density of the solution and d_{wet} is diameter of the wet particle. This equation connects the particle properties (size, surface tension, density and water activity) with the thermodynamic state of the surroundings (temperature, saturation ratio) (**Paper II**).

3 Measurement and methods

This thesis included data analysis from two field measurement stations in Finland, and one chamber experiment conducted in Germany, see the locations of the sites in Fig. 3. In addition, numerical modeling was also used for the simulation of the chamber experiments. In the following, we will introduce these measurement and methods in this section.

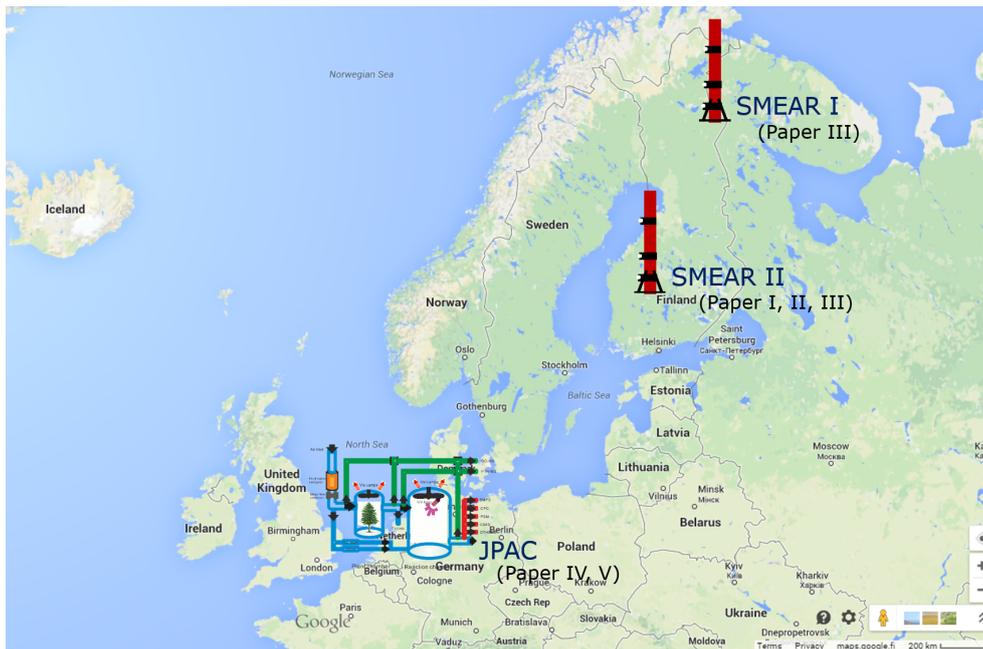


Figure 3: A map (Google map) illustrating locations of the field measurement stations and the chamber experiment.

3.1 Atmospheric field measurements

A large part of the dataset in this thesis is based on the continuous measurements at two Finnish SMEAR stations (Station for Measuring Ecosystem-Atmosphere Relations (Hari and Kulmala, 2005)): SMEAR I ($67^{\circ}46'N$, $29^{\circ}35'E$, 400 m a.s.l.) in Värriö (**Paper III**), and SMEAR II ($61^{\circ}51'N$, $24^{\circ}17'E$, 170 m a.s.l.) in Hyytiälä (**Paper I–III**), Finland.

The SMEAR I station is located inside the Arctic Circle, emphasizing research on interactions between trees and atmosphere, air quality and aerosols, and is less than 200 km from the Russian emission sources of Kola Peninsula. The station has been operated since 1991, offering long time-series of gas and aerosol parameters, and meteorological parameters. We used a 13-year dataset from 1998 to 2010 in **Paper III**.

The SMEAR II station is the most comprehensively equipped SMEAR station, to study the material and energy flows in the atmosphere-vegetation-soil continuum at different temporal and spatial scales. The terrain of the site represents the boreal coniferous forest, which covers about 17 % of the Earth’s land surface. The over 40-year old Scots pines (*Pinus sylvestris*) dominated the vegetation layer with some Norway spruces (*Picea abies*) and Silver birches (*Betula pendula*) around the station, and the average tree height is around 16 meters. The operation of the SMEAR II station has been ongoing since 1995. Long time-series for gas and aerosol parameters, meteorological parameters (temperature, RH, O₃, SO₂ etc.) are readily accessible. Measurements on BVOC fluxes and concentrations were also performed. We used a 4-year dataset in **Paper I**, a one-year dataset from mid-2008 to mid-2009 in **Paper II**, and a 15-year dataset between 1996 and 2010 in **Paper III**.

3.1.1 Instruments

Many instruments, used over long time spans at both SMEAR stations, have proven to be well suited for the research carried out in this study. With the large amount of data obtained from these measurements in this study, we were able to investigate some key parameters and potential mechanisms in the ‘vegetation-aerosol-climate’ system. The main instruments used in this work are listed as following:

Differential Mobility Particle Sizer (DMPS) measures the aerosol particle number size distribution (Aalto et al., 2001). The setup of the DMPS system combines a Differential Mobility Analyzer (DMA) and a Condensation Particle Counter (CPC), see the schematic picture of one DMPS system illustrated in Fig. 4. The DMA sizes aerosol particles based on their electrical mobility. The CPC detects the total number concentration of aerosol particles larger than a certain cut-off size. This cut-off size depends on the instrumental design combining the condensation and optical techniques. The particles are firstly charged by a radioactive neutralizer, in order to gain a well-defined Boltzmann charge distribution, and then they are sized by the DMA.

After that the selected particles are detected by the CPC.

The DMPS system measured the number concentrations of particles with diameter from 3 nm to 1 μm at the SMEAR II station since the operation of the station (Aalto et al., 2001), whereas particles in size range 8–460 nm were measured before April 2003 at the SMEAR I station, and then was extended to the same particle size range as in the SMEAR II station (Dal Maso et al., 2007). The dataset of the particle number size distributions measured at the SMEAR II station were used in **Paper I–III** with several different selected time periods. The DMPS data measured at the SMEAR I station were used in **Paper I**.

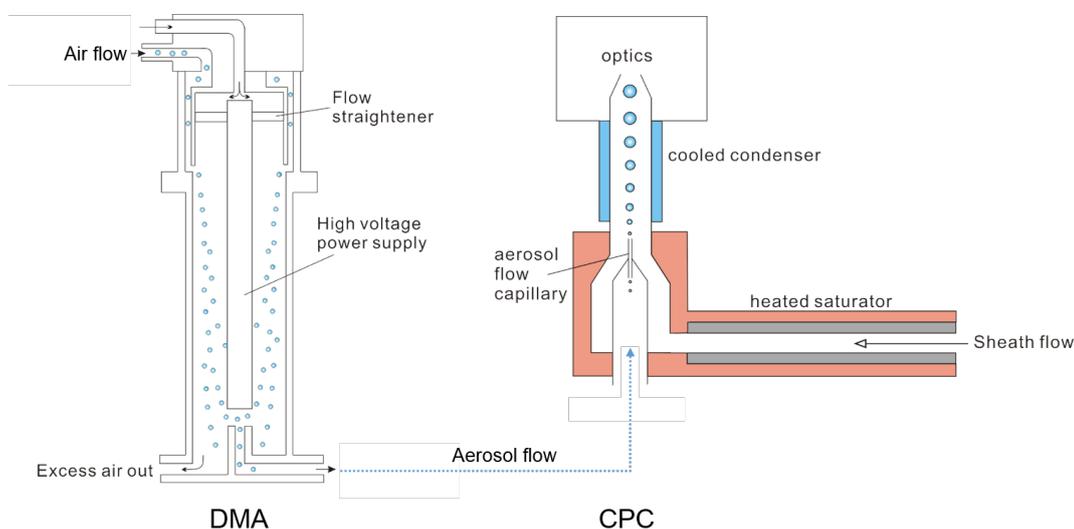


Figure 4: A schematic picture of the DMPS (Differential Mobility Particle Sizer) system, including a DMA (Differential Mobility Analyzer) connected with a CPC (Condensation Particle Counter).

Proton Transfer Reaction Mass Spectrometry (PTR-MS) is an online instrument which measures the concentrations of volatile organic compounds in ambient air (Lindinger et al., 1998). The PTR-MS was used to study the long-term VOC measurement at the SMEAR II station. The technical calibration and stability of the PTR-MS together with the equations to derive the VOC concentrations were described in detail by Taipale et al. (2008). The detection limit of PTR-MS for monoterpenes was 0.01 ppbv. We used the PTR-MS dataset from 2006 to 2009 in **Paper I**. In addition, the PTR-MS was used to measure the VOC concentrations from the JPAC chamber

experiment, and its data were analyzed in **Paper V**.

Aerosol Mass Spectrometer (AMS) detects the mass concentrations of species including sulfate, nitrite, chloride, ammonium and organic compounds in the submicron aerosol particles (Canagaratna et al., 2007). One Aerodyne Time-of-Flight AMS was used in campaign-wise measurements at the SMEAR II station, and the AMS data were used in a case study in **Paper I**.

Cloud Condensation Nuclei Counter (CCNC) measures the concentrations of the cloud condensation nuclei (Roberts and Nenes, 2005). One CCNC was installed at ground level at the SMEAR II station, and it was operated at water super-saturations of 0.1–1.0 %. Together with CCNC, a **Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA)** (Ehn et al., 2007) was used to detect the hygroscopicity of aerosol particles in **Paper II**.

3.1.2 Backward trajectories

In addition to the measurements, backward trajectories were used in one of the studies in the “averaged air parcel history” method (**Paper III**). The hourly 96-hour backward trajectories arriving at the SMEAR I and the SMEAR II stations were calculated with the HYSPLIT4 model (Draxler and Hess, 1998). Each individual travel point of the backward trajectory includes the air temperature at the traveling height, mixing layer height, solar flux, precipitation, pressure and relative humidity. The meteorological data in the trajectory calculations was from a global data assimilation system (GDAS) reanalysis archive for data sets after 2004, and from an final (FNL) archive for data sets before 2004, provided by the NCEP (National Centre of Environmental Predictions). Previous studies have shown uncertainty of the trajectory calculations to be 10–30 % of the travel distance (Draxler and Hess, 1998). The uncertainty of the meteorological data has been minimized in the GDAS and FNL reanalysis archives.

3.2 Jülich Plant Atmosphere Chamber

We used the dataset from one chamber experiment campaign conducted at the Jülich Plant Atmosphere Chamber (JPAC) located in Forschungszentrum Jülich, Germany (**Papers IV–V**). Compared with the field observations, one main advantage of this

chamber experiment is that the climatic parameters can be artificially controlled, which provides an ideal near-ambient atmosphere environment for the purpose of investigating the potential mechanisms of secondary particle formation from biogenic tree emissions. For example, changing temperature and photosynthetic photon flux density in the plant chamber could cause change in the tree emission strengths and thus change the BVOC source strengths in the reaction chamber. The JPAC chamber setup utilized several cutting-edge instruments which can directly measure freshly formed aerosol clusters, thus it may allow us to determine the mechanisms of nucleation and growth of aerosol particles from tree emitted BVOCs. However, such ‘ideal’ system has its natural drawbacks, i.e. the chamber is isolated with glass walls, and such artificially introduced chamber wall effects may result in a different aerosol formation mechanism (**Paper IV**), compared to the ambient field measurements.

The details related to the JPAC chamber facility can be found from e.g. Mentel et al. (2009), Schimang et al. (2006), and **Paper V**. Fig. 5 describes the basic setup of the JPAC facility. In brief, the JPAC system consists of two borosilicate glass chambers with Teflon floors. A small chamber (1150 L) was used as the plant chamber, in which three small trees including pine, Norway spruce, and Silver birch were planted. The small chamber was connected to the larger chamber that worked as reaction chamber (1450 L, surface to volume ratio of 4.87 m^{-1}), which allowed the loading of tree emissions into the reaction chamber, where O_3 was directly loaded and OH was generated by periodically activated UV light. Discharge lamps were used for the illumination to simulate the solar light spectrum in both chambers.

Several instruments were connected to the plant chamber and reaction chamber to measure both gas- and particle-phase components. Temperature, relative humidity (RH), concentrations of O_3 , CO_2 and H_2O were measured by commercial analytical instruments. The VOC concentrations from C_5 to C_{20} in the outflow air from the plant chamber were measured by one Gas Chromatography Mass Spectrometers (GC-MS) (Heiden et al., 2003), another GC-MS was used to identify the OH concentration by determining the decrease in the concentration of a tracer compound in the reaction chamber (Kiendler-Scharr et al., 2009). In addition, VOC concentrations in both chambers were continuously measured by an on-line Proton Transfer Reaction Mass Spectrometer (PTR-MS). The gas phase H_2SO_4 concentration in the reaction chamber was measured by a CIMS (Petäjä et al., 2009). Similar to the DMPS, a Scanning Mobility Particle Sizer (SMPS) was used to measure particle number size distributions

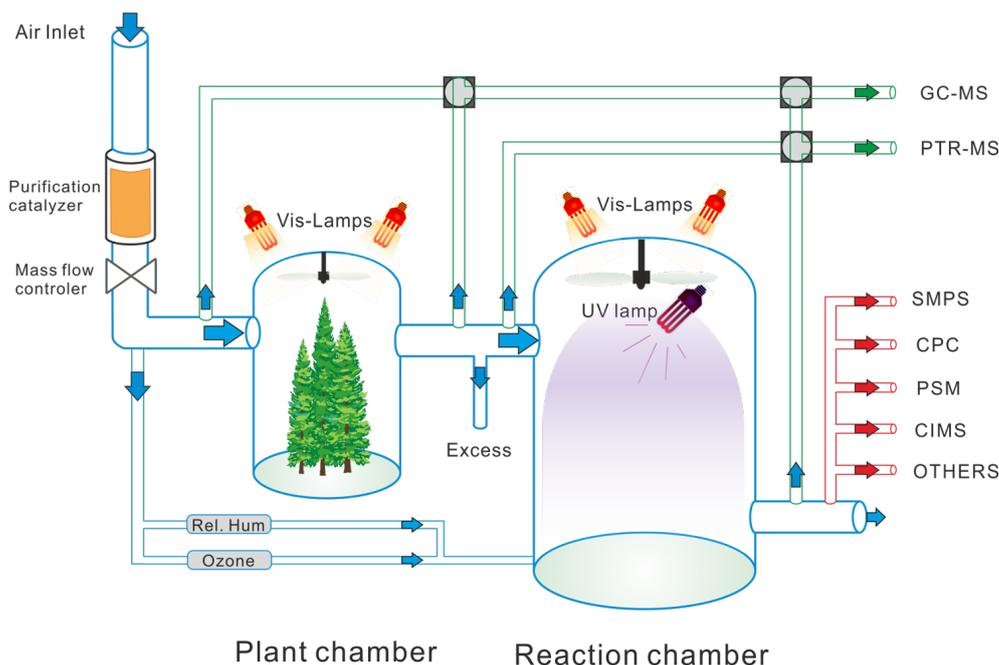


Figure 5: A schematic picture of the setup of the Jülich Plant Atmosphere Chamber (JPAC). The JPAC consists of two glass chambers with Teflon floors: the small one served as the plant chamber, and the larger one served as the reaction chamber.

in size range between 14 and 600 nm. The total number of particles larger than 7 nm were measured by a condensation particle counter (CPC). The total number of particles larger than 1.6 nm in diameter was measured by a Particle Size Magnifier (PSM, Airmodus A09 prototype) with cut-off size being around 1.6 nm.

3.3 MALTE-BOX model (Atmospheric simulation/modeling)

Numerical model was used in this study to investigate some potential processes behind the secondary particle formation. The main model used was the MALTE ((Model to predict new Aerosol formation in the Lower TropospherE) model, developed by Boy et al. (2006). MALTE is a one-dimensional model, and we used several modules from the original code as the MALTE-BOX model, which consisted of main modules for air chemistry, aerosol dynamics, and chamber wall losses. The structure of the MALTE-BOX model is illustrated in Fig. 6.

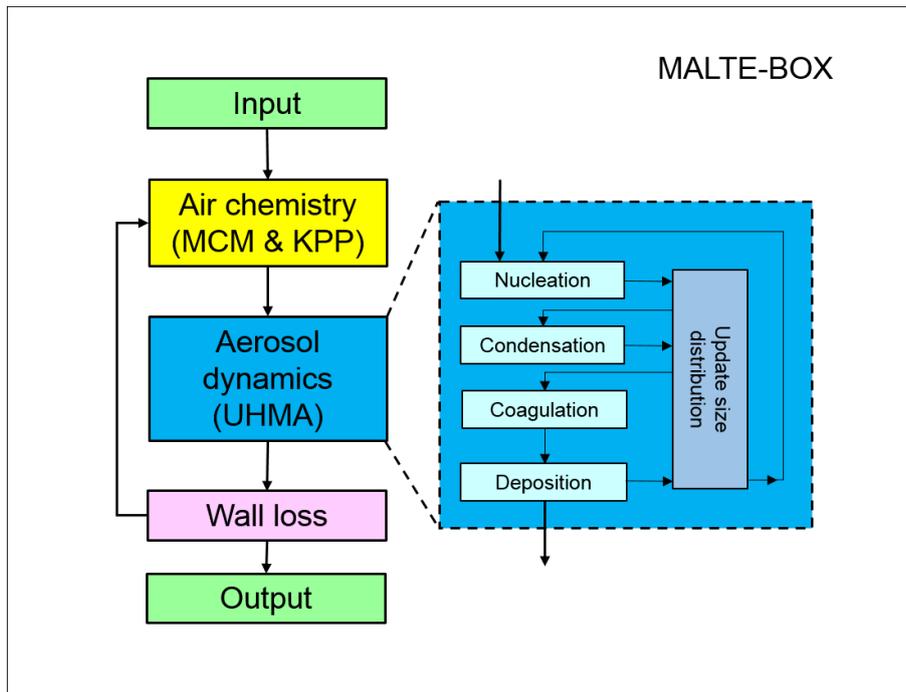


Figure 6: A schematic figure of the structure of the MALTE-BOX model, the structure of the aerosol dynamics module (UHMA, University of Helsinki Multicomponent Aerosol model) is illustrated in the right blue panel.

The chemical reaction equations were selected from the Master Chemical Mechanism (MCM) v3.2 (Jenkin et al., 1997, 2012), and calculations of the air chemistry were solved via Kinetic Pre-Processor (KPP) version 2.1 (Damian et al., 2002).

The aerosol dynamic processes including nucleation, condensation, evaporation and coagulation were calculated using the size-segregated UHMA model (University of Helsinki Multicomponent Aerosol model (Korhonen et al., 2004)), implemented in the MALTE-BOX model as a module. The original UHMA code included both activation nucleation and kinetic H_2SO_4 nucleation mechanisms (Eq. 2 and 3). We updated the UHMA code to include the organic nucleation (Eq. 4) with the purpose of testing the differences in particle formation rates after the introduction of VOCs.

The original MALTE-BOX model included two parameterizations for particle wall losses: one from Crump and Seinfeld (1981) for mono-dispersed particles, and another from Park et al. (2001) for poly-dispersed particles. The wall deposition for gas com-

pounds was also calculated from Park et al. (2001).

Studies suggested that some VOC gas losses on chamber surfaces are reversible during the chamber experiments (Zhang et al., 2014; Kokkola et al., 2014; Roldin et al., 2014). Therefore, we coupled a gas-wall partitioning mechanism in the original MALTE-BOX code in this study, which calculates the adsorption and desorption of SVOCs on the chamber surfaces. This reversible process of SVOCs was modeled by the following equation (Matsunaga and Ziemann, 2010):

$$k_{w,g,i} = \frac{k_{g,w}}{(RT/p_{0,i}C_w/(M_w\gamma_{w,i}))} \quad (8)$$

where $k_{g,w}$ (s^{-1}) is the first order loss rate from the gas phase to the chamber walls, $k_{w,g}$ (s^{-1}) is the desorption rate of SVOCs from the chamber surfaces out to the gas phase, C_w is an effective wall equivalent mass concentration of solvent which the organic compounds can dissolve into, M_w is the average molar mass of the solvent on the walls, and $\gamma_{w,i}$ is the activity coefficient of compound i in the solvent.

4 Results and discussions

4.1 Connection between monoterpenes and aerosol particles from anthropogenic origin

Monoterpene emission measured at the SMEAR II station is temperature dependent, with diurnal and seasonal variations (Hakola et al., 2003; Lappalainen et al., 2009). However, visual inspection on the time-series of the monoterpene concentrations measured at the SMEAR II station revealed peaks of extremely high levels. Fig. 7 illustrates an example of the monoterpene concentrations measured on 8 March 2007 together with the particle size distribution observations (a similar case is also depicted in Fig. 2). These extremely high monoterpene concentrations were considered as the monoterpene pollution episodes, and were examined in details in **Paper I**. We found that the origin of these monoterpene episodes was mainly the Korkeakoski sawmill, ca. 6 km from the SMEAR II station. Overall, this origin resulted in over 30 % increase in the local average monoterpene concentrations.

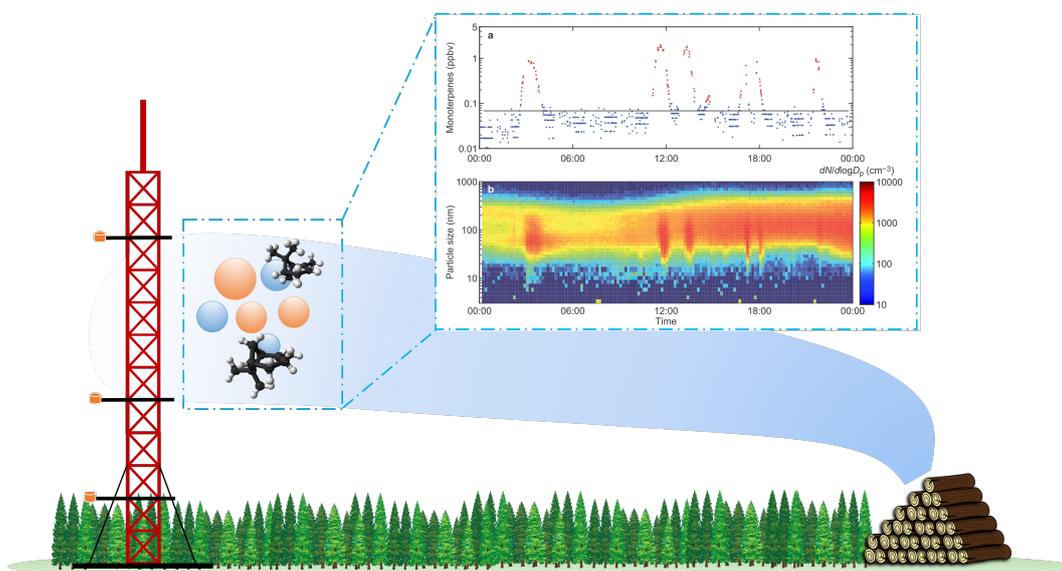


Figure 7: A schematic picture of the monoterpene pollution episodes in association with elevated aerosol particle number concentrations observed on 8 March 2007 at the SMEAR II station, Hyytiälä, Finland. The Korkeakoski sawmill is located ca. 6 km away from the SMEAR II station towards 130° Northwest.

Co-occurred with the increase in anthropogenic originated monoterpenes, a large amount of aerosol particles were observed simultaneously (see in Fig. 7), resulted in a noticeable local aerosol loading. The composition of these particles were examined, and there was no clear difference compared with the local background particles, where the background aerosol particle masses were mostly dominated by the secondary organic aerosol contributed from regional sources, e.g. biogenic SOA from tree emissions (Raatikainen et al., 2010). Therefore, monoterpenes, regardless their biogenic or anthropogenic origins, contributes to the production of secondary organic particles after atmospheric oxidations. The aerosol particles formed during anthropogenic monoterpene episodes were large enough to act as CCN. **Paper II** presented the seasonal variation of the CCN concentrations measured at the SMEAR II station.

In addition to our finding, Hakola et al. (2012) presented the distribution of BVOCs from the species-speciated BVOC measurement by GC-MS at the SMEAR II station, and found that the concentrations of camphene and p-cymene have shown particular high levels during the monoterpene pollution episodes. Also, Vestenius et al. (2014) suggested possible increase in associated acidic reaction products of monoterpenes during these episodes at the SMEAR II station.

4.2 Linking the biogenic monoterpene emissions and natural aerosol production

The anthropogenic origin largely contributes to the local monoterpene budget and the corresponding SOA production. However, SOA formation from biogenic emissions dominates the global aerosol budget. We investigated the natural aerosol evolution as function of biogenic monoterpene emissions in **Paper III**, using the “averaged air parcel history” method, developed by Tunved et al. (2006, 2008). Fig. 8 illustrates the concept of this method. We chose trajectories from clean area with minimum anthropogenic influence, and confined the estimated biogenic monoterpene emissions in the boundary layer during the air mass transport.

We found that secondary aerosol particles were freshly formed via nucleation when clean air originally from the ocean entered the land, after which these particles continuously grew to larger sizes during the air mass transport. The observed aerosol masses at the receptor stations have shown linear correlation with the travelling time-over-land of the

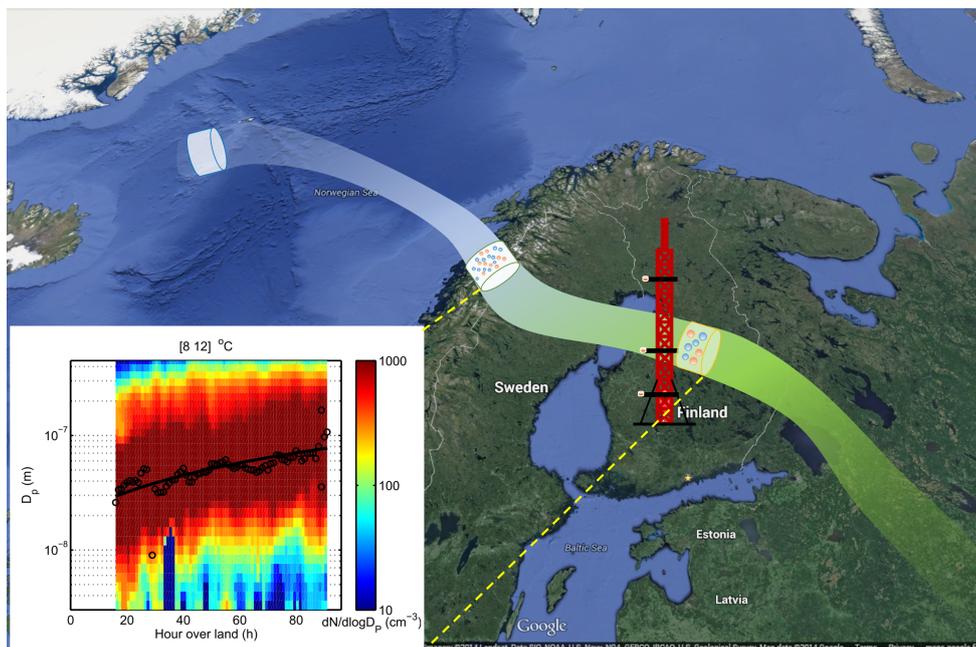


Figure 8: A conceptual figure of the observed aerosol particle size evolution along the back trajectories. For detailed information about calculation and selection of the backward trajectories, see **Paper III**.

air parcels, similar to the findings by Tunved et al. (2006) and Väänänen et al. (2013). The average particle mass gain per hour were $0.02 \mu\text{g m}^{-3}$ at the SMEAR I station, and $0.04 \mu\text{g m}^{-3}$ at the SMEAR II station. We discussed the connection between the accumulated biogenic monoterpene emissions and the number concentrations of particles in three size-modes. The total particle number concentration at the accumulation mode showed positive correlation with the accumulated biogenic monoterpene emissions. However, the nucleation mode particle number concentrations did not positively correlate with the monoterpene emissions, indicating that nucleation was suppressed by the large condensation sink of accumulation mode particles resulted from the higher monoterpene emissions.

4.3 Temperature response of the natural aerosol production potential

Temperature plays a double role in the ‘vegetation-aerosol-climate’ system first by acting as a determining factor involved in the system, and secondly as a result of the feedback of the system. Higher temperature enhances the BSOA formation (Day and Pandis, 2011; Leaitch et al., 2011; Paasonen et al., 2013), whereas the exact relation between the temperature, BSOA production and natural CCN concentration levels remains uncertain. Temperature influences not only the precursor emissions of BSOA, but also the atmospheric oxidation reaction rates, resulting in gas-particle partitioning and potential heterogeneous reaction in the particle phase (Kroll and Seinfeld, 2008; Hallquist et al., 2009; Riipinen et al., 2012). With the help of the back trajectory method, we studied the potential temperature influence on the natural aerosol budget from estimated biogenic monoterpene emissions during air mass transport in **Paper III**. Overall, temperature showed an indirect effect when we studied the particle concentrations with respect to both biogenic monoterpene emissions and temperature, i.e. the observed particle concentrations in larger sizes were determined by the amount of monoterpenes emitted in the air mass, which is dependent on temperature.

We obtained the apparent **aerosol yield** from the linear fittings between the observed aerosol mass at the receptor sites and the cumulative monoterpene emissions. Fig. 9 illustrates the apparent aerosol yield as a function of the temperature in five ranges. The apparent aerosol yield decreased with an increasing temperature at the SMEAR II station. However, the average aerosol yield at the SMEAR I station was different, in which it was smaller in the first two temperature bins than in the next two temperature bins. The variation in the estimated apparent aerosol yields was quite large as a function of the temperature parameter and the site. Nevertheless, two features are evident in the aerosol yield estimation: firstly aerosol mass production in cooler temperatures is more efficient for the SMEAR II station, and the efficiency of VOC transformation is higher at this more southern station. Secondly, at higher average temperatures, the apparent aerosol yield from monoterpenes at both stations started to approach values close to each other.

Overall, results in **Paper III** suggest that the temperature dependence of BSOA production should be treated with caution. One should avoid using a simple parameterization in predicting the aerosol production potential from rising temperatures in

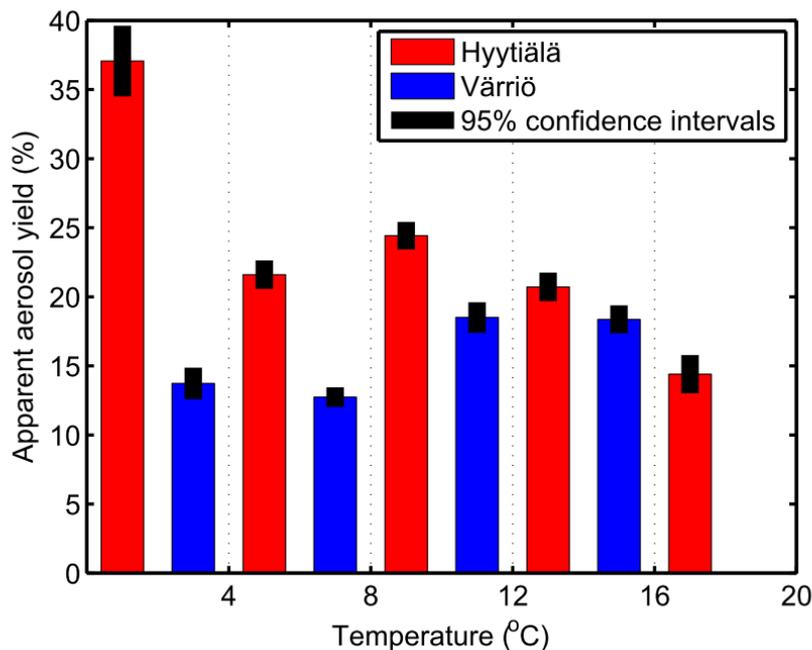


Figure 9: Estimated apparent aerosol yield (i.e. the direct fitting slope between aerosol mass and total monoterpene emission) in five temperature bins both at the SMEAR I station (blue bars) and the SMEAR II station (red bars). The black bars indicate 95 % confidence intervals from the fitting slopes at both stations.

future. Further investigation on the detailed processes of BSOA yield as a function of temperature is necessary to discuss the actual aerosol distribution and its climate effects.

4.4 Simulation of the new particle formation from tree emissions in JPAC chamber

Paper I and **Paper III** showed clear connection between monoterpenes and secondary particle formation based on the field observations. To closer look at the mechanisms behind the relation of these two aspects, we performed numerical simulation on the new particle formation events observed in the JPAC chamber experiments (**Paper IV**), aiming to firstly identify the potential participation of BVOCs in the new particle formation process; and secondly to quantify the relative contribution of terpene

oxidation products to the SOA production. Fig. 10 illustrates the occurrences of the main processes in the JPAC reaction chamber, including gas phase chemistry, aerosol dynamics, and gas-wall-partitioning of SVOCs, which have been simulated using the MALTE-BOX model.

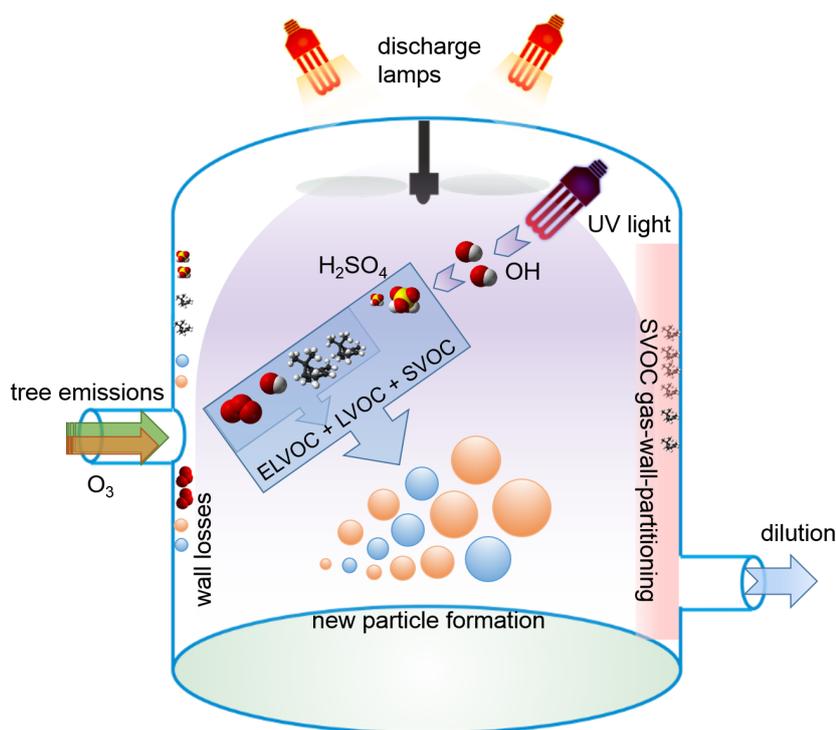


Figure 10: A conceptual figure summarizing the series of gaseous chemical reactions and aerosol dynamics of observed new particle formation events in the JPAC reaction chamber.

The concentrations of gas compounds modeled have shown good agreements with the measurements. OH was formed once the UV light was turned on in the JPAC reaction chamber, OH concentration modeled and measured agreed within a factor of two, which was ca. $7 \times 10^7 \text{ cm}^{-3}$ on average. Then H_2SO_4 was substantially formed from OH oxidation with SO_2 . We found two increase peaks of H_2SO_4 concentration from the measurement, whereas the model was not able to fully predict the second increase with Criegee intermediate included chemistry. The modeled O_3 concentration was within 10–20 % from the measurement. Monoterpene concentrations predicted from the model

correlated well with the total monoterpene concentrations detected by PTR-MS. Thus it is reasonable to use the modeled monoterpene concentrations and their oxidation products for the particle phase simulation.

We used two nucleation mechanisms for the particle phase simulation including both kinetic H_2SO_4 nucleation and organic nucleation. The nucleation coefficient used for kinetic H_2SO_4 nucleation was $2.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, and the organic nucleation coefficient was $9.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. In addition, we used a simplified gas-particle partitioning method which classifies the terpene oxidation products into either ELVOCs or SVOCs for particle condensational growth, and the gas-wall-partitioning of SVOCs was calculated by Eq. 8. The resulting particle size distributions from the aerosol dynamics simulation are illustrated in Fig. 11. One can see that the particle number concentrations modeled by the organic nucleation gradually decreased from Day-1 to Day-4 during the UV-on periods, similar to the SMPS measurements, whereas an opposite relation was seen from the particle number size distributions modeled by the H_2SO_4 nucleation. Also, the modeled particle size distributions by the organic nucleation showed better agreement with the measurements during the UV-off periods, as the particle number concentration was over-predicted by the kinetic H_2SO_4 nucleation.

The modeled results in **Paper IV** showed that a substantial amount of SVOCs adsorbed on the JPAC reaction chamber walls during the measurement campaign, and the desorption of SVOCs became substantial after Day-1. Comparing with the modeled particle number size distributions without considering the SVOC gas-wall-partitioning (Fig. 11b, d), it is conclusive that the desorption of SVOCs from the walls significantly contributed to growth of the freshly formed particles to larger sizes (Fig. 11c, e). We further looked at the composition of the aerosol particles, results showed that ELVOCs and SVOCs approximately equally contributed to particle volume production, but ELVOC exclusively grew the smallest particles.

The MALTE-BOX model was capable of predicting the average concentrations of both gas and particle phase components as the measurements within a factor of 1–2, yet the whole distribution did not show full agreement between modeled results and the measurements. Therefore, to better understand the processes in the JPAC chamber, it is important to include explicit description of air chemistry calculations and gas-wall-partitioning. We simplified the calculations of particle condensational growth using representative model compounds. To better recognize the actual gas-particle partitioning, it is necessary to include all condensable vapor precursors with their

saturation vapor pressure information in future studies.

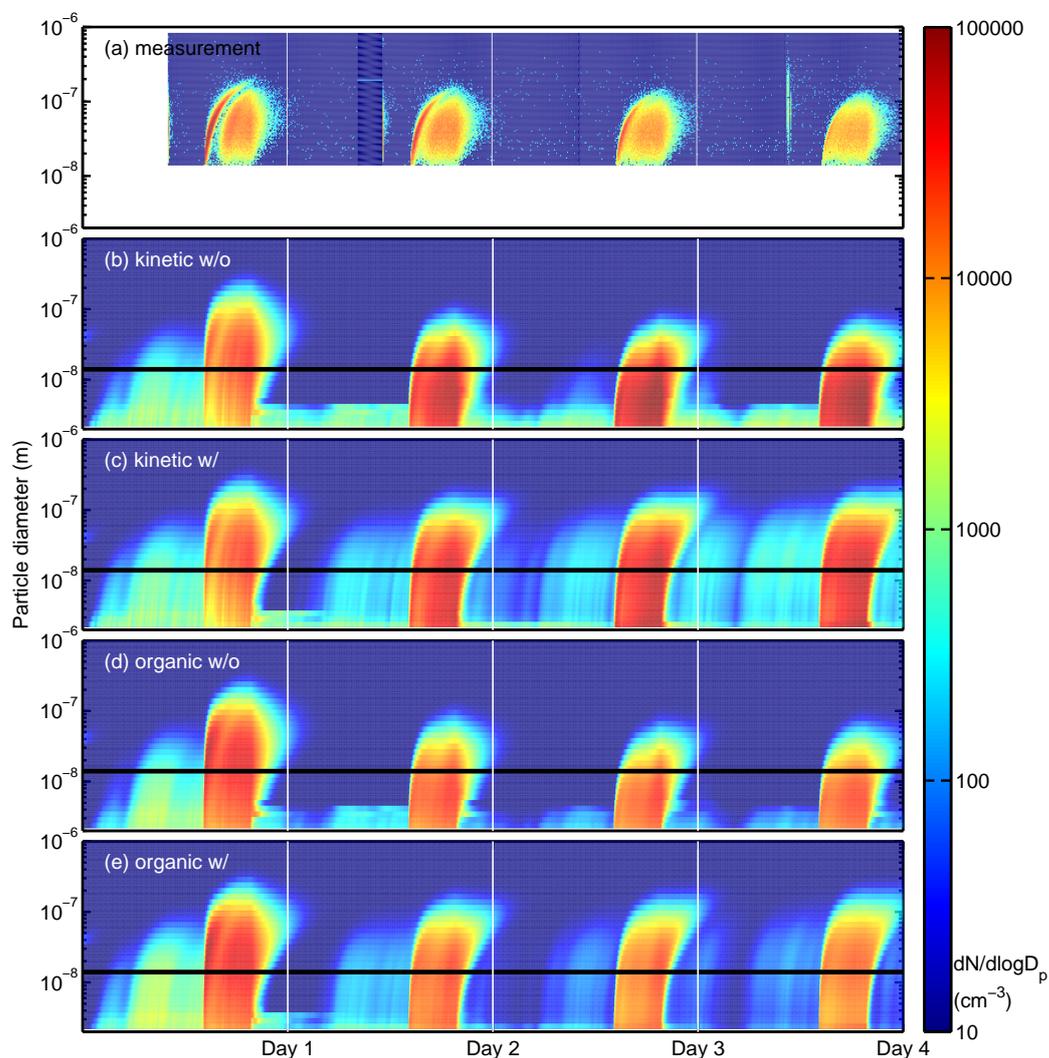


Figure 11: Contour plots of aerosol particle number size distributions as function of time from the SMPS measurements (a), from the MALTE-BOX model predicted by kinetic H_2SO_4 nucleation without SVOC gas-wall-partitioning (b) and with SVOC gas-wall-partitioning walls (c); from the model by organic nucleation without SVOC gas-wall-partitioning (d) and with SVOC gas-wall-partitioning (e). The black lines indicate the smallest particle size measured by SMPS.

5 Review of papers and the author’s contribution

The author is solely responsible for the introduction of this thesis.

Paper I studied the anthropogenic origin of monoterpenes observed at the SMEAR II station. We quantitatively examined the anthropogenic contributions to the measured monoterpene concentrations. We discussed the correlation between the increased monoterpene concentrations and co-occurring aerosol particles in terms of both number and volume concentrations, and we also analyzed the chemical compositions of these co-occurred particles through case studies. I was responsible for the whole data analysis and I wrote most of the paper.

Paper II investigated the seasonal distribution of cloud condensation nuclei (CCN) concentrations in a boreal forest environment, using a one-year CCN measurements together with the hygroscopicity measurements. We also analyzed the effect of new particle formation events on the CCN production. In this paper, I participated in data analysis, produced four figures for the paper, and contributed commenting the paper.

Paper III presented the temperature influence on the natural aerosol formation and mass yield over boreal forest, using an “averaged air parcel history” method. We discussed the correlation between the estimated biogenic monoterpene emissions and particle number concentrations, we estimated the particle losses during air mass transport, and we discussed the apparent aerosol yield as a function of temperature. In this paper, I made all the data analysis and wrote most of the paper.

Paper IV investigated the mechanisms of new particle formation observed in the Jülich Plant Atmosphere Chamber (JPAC) experiments, through measurements and simulations of the MALTE-BOX model with near-explicit air chemistry and aerosol dynamics. We performed simulations on both gas- and particle-phase components. We compared results modeled by two nucleation mechanisms (kinetic H_2SO_4 nucleation and organic nucleation), and discussed the importance of SVOC gas-wall-partitioning in chamber experiments. I was responsible for modification and implementation of the MALTE-BOX model, performing the model simulations, and analyzing all the data. I wrote most of the manuscript.

Paper V presented data analysis of the JPAC experiments to study the influence of boreal tree-emitted BVOCs and sulfuric acid on nanoparticle formation rates at

ambient concentration levels. The particle formation rates were derived separately from particle growth rates, and the formation mechanism of nano-CN was discussed. In this paper, I was responsible for a large part of the data analysis. I made most of the figures, and commented on the manuscript.

6 Conclusions

The work of this thesis attempts to analyze the source, the formation and growth mechanisms, and the sink of secondary particle formation from the contribution of tree emitted VOCs, and to test the overall temperature response in the ‘vegetation-aerosol-climate’ system. This work utilized both long-term field observations and campaign-wise chamber experiments, as well as numerical model. In conclusion, we found that:

1. Monoterpenes, considered as one of the main precursors of SOA production, originate not only from biogenic emissions, but also from anthropogenic sources (e.g. forest industry). The anthropogenic origin can significantly elevate the local or regional monoterpene concentrations. The oxidation products of monoterpenes contribute to the secondary organic particles formation, regardless of the origins of monoterpenes, since aerosol particles co-occurred with anthropogenic monoterpenes had similar chemical compositions as the background particles in a boreal forest environment. With large contribution from monoterpene oxidation products, secondary particles usually grew large enough to act as CCN, which could contribute to the local or regional cloud production.

2. Monoterpenes from biogenic emissions showed direct link to the secondary organic particle production. With the help of an “averaged air parcel history” method, we found that secondary aerosol particles were freshly formed via nucleation when clean air from the ocean entered the land. Then the nucleated particles continuously grew to larger sizes due to condensation of the oxidation products of biogenic emissions accumulated along air mass transport. The observed aerosol mass at the receptor stations has shown linear correlation with the air parcel travelling time-over-land, i.e. secondary aerosol mass correlates with the accumulated monoterpene emission along the air mass transport.

3. The ‘vegetation-aerosol-climate’ system is very complicated. We tested the temperature response by linking vegetation (monoterpene emission), aerosol (aerosol mass production), and climate system (CCN), using an “averaged air parcel history” method. We showed that both the travelling time-over-land and air temperature affect the evolution of the natural aerosol production. Although the nucleation mode particle number concentrations were higher at lower temperatures, particle number concentrations at accumulation mode showed positive relation to the temperature, suggesting that more efficient CCN production was associated with the BSOA production at higher tem-

perature. Our results suggested that direct temperature effect on particle formation process is minor, but temperature effect on the biogenic emissions resulted in an indirect influence on the BSOA production and corresponding CCN formation.

4. The analysis of the new particle formation from a JPAC chamber experiment showed that the particle formation rate was proportional to the H_2SO_4 and biogenic VOC emission, in relation to a mechanism that nucleating BVOC oxidation products are rapidly formed and activated with H_2SO_4 . A numerical simulation was performed with the same experiments, which further confirmed that H_2SO_4 is a critical compound in the nucleation process, however nucleation involving the oxidation products of BVOC and H_2SO_4 better explains the nucleation mechanism (i.e. the organic nucleation). Both findings are in line with the latest results from e.g. Schobesberger et al. (2013), Ehn et al. (2014), Kulmala et al. (2014b), and Riccobono et al. (2014), in which several instruments can directly detect the size and composition of freshly formed aerosol clusters and their precursors. However, all these findings were from the well-controlled chamber experiments with limited chemical complexity. Even though our results were based on the near ambient levels of atmospheric concentration and mixtures, the simulation could not identify any specific VOC compounds participating in the initial steps of nucleation. Therefore, the actual nucleation mechanism in the ambient environment remains uncertain.

5. Atmospheric chamber experiments are very useful to investigate some specific mechanisms related to the ‘vegetation-aerosol-climate’ system, as one can carefully control the climatic parameters, and target specific questions of interest. However, one should pay special attention to the wall effects during the chamber experiment, as we have found that the chamber surfaces constitute the major net sink of semi-volatile organic compounds at the start of the experiment, but this wall uptake gradually reduced because of desorption of the compounds. Thus, in order to capture the observed temporal evolution of the particle number size distribution, we had to consider a reversible gas-wall partitioning for the model simulation.

The process of secondary particle formation is complicated, firstly because the mechanism is not well understood, and secondly because such process is linked to the Earth system. In this study, we tested both the mechanism of homogeneous nucleation, and the feedback to the ‘vegetation-aerosol-climate’ system, also we showed changes of secondary particle formation due to human activity. Although we have used analysis from comprehensive long-term field measurements and chamber experiments, as well as up-

to-date numerical model, we are still not able to conclude the mechanisms behind the phenomena we observed. Therefore, to be able to fully reveal the secondary particle formation process and its linkage to the climate system, it is encouraging to continue the aerosol research by developing more cutting-edge instruments, and advancing comprehensive numerical models.

References

- Aalto, P., Hameri, K., Becker, E., Weber, R., Salm, J., Makela, J. M., Hoell, C., O'Dowd, C. D., Karlsson, H., Hansson, H. C., Vakeva, M., Koponen, I. K., Buzorius, G., and Kulmala, M. (2001). Physical characterization of aerosol particles during nucleation events. *Tellus Ser. B*, 53(4):344–358.
- Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurten, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppa, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Trostl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J. (2013). Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere. *Nature*, 502(7471):359–363.
- Anderson, T. L., Charlson, R. J., Schwartz, S. E., Knutti, R., Boucher, O., Rodhe, H., and Heintzenberg, J. (2003). Climate forcing by aerosols - a hazy picture. *Science*, 300(5622):1103–1104.
- Andreae, M. O. and Crutzen, P. J. (1997). Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science*, 276(5315):1052–1058.
- Andreae, M. O., Jones, C. D., and Cox, P. M. (2005). Strong present-day aerosol cooling implies a hot future. *Nature*, 435(7046):1187–1190.
- Andreae, M. O. and Rosenfeld, D. (2008). Aerosol-cloud-precipitation interactions. Part 1. the nature and sources of cloud-active aerosols. *Earth-Sci. Rev.*, 89(1-2):13–41.
- Arneth, A., Unger, N., Kulmala, M., and Andreae, M. O. (2009). Clean the air, heat the planet? *Science*, 326(5953):672.

- Ayers, G., Cainey, J., Gillett, R., Saltzman, E., and Hooper, M. (1997). Sulfur dioxide and dimethyl sulphide in marine air at Cape Grim, Tasmania. *Tellus Ser. B*, 49(3):292–299.
- Bertin, N., Staudt, M., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Fugit, J. L., and Torres, L. (1997). Diurnal and seasonal course of monoterpene emissions from *Quercus ilex* (L.) under natural conditions - Applications of light and temperature algorithms. *Atmos. Environ.*, 31:135–144.
- Bonn, B. and Moortgat, G. K. (2003). Sesquiterpene ozonolysis: Origin of atmospheric new particle formation from biogenic hydrocarbons. *Geophys. Res. Lett.*, 30(11).
- Boy, M., Hellmuth, O., Korhonen, H., Nilsson, E. D., ReVelle, D., Turnipseed, A., Arnold, F., and Kulmala, M. (2006). MALTE - model to predict new aerosol formation in the lower troposphere. *Atmos. Chem. Phys.*, 6:4499–4517.
- Boy, M., Mogensen, D., Smolander, S., Zhou, L., Nieminen, T., Paasonen, P., Plass-Dülmer, C., Sipilä, M., Petäjä, T., and Mauldin, L. (2013). Oxidation of SO₂ by stabilized Criegee intermediate (sCI) radicals as a crucial source for atmospheric sulfuric acid concentrations. *Atmos. Chem. Phys.*, 13(7):3865–3879.
- Boy, M., Rannik, U., Lehtinen, K., Tarvainen, V., Hakola, H., and Kulmala, M. (2003). Nucleation events in the continental boundary layer: Long-term statistical analyses of aerosol relevant characteristics. *J. Geophys. Res. -Atmos*, 108(D21).
- Cahill, T. M., Seaman, V. Y., Charles, M. J., Holzinger, R., and Goldstein, A. H. (2006). Secondary organic aerosols formed from oxidation of biogenic volatile organic compounds in the Sierra Nevada Mountains of California. *J. Geophys. Res. -Atmos*, 111(D16).
- Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R. (2007). Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrom. Rev.*, 26(2):185–222.
- Carslaw, K. S., Boucher, O., Spracklen, D. V., Mann, G. W., Rae, J. G. L., Woodward, S., and Kulmala, M. (2010). A review of natural aerosol interactions and feedbacks within the earth system. *Atmos. Chem. Phys.*, 10(4):1701–1737.

- Covert, D. S., Kapustin, V. N., Quinn, P. K., and Bates, T. S. (1992). New particle formation in the marine boundary layer. *J. Geophys. Res. -Atmos*, 97(D18):20581–20589.
- Crump, J. G. and Seinfeld, J. H. (1981). Turbulent deposition and gravitational sedimentation of an aerosol in a vessel of arbitrary shape. *J. Aerosol Sci.*, 12(5):405–415.
- Dal Maso, M., Sogacheva, L., Aalto, P. P., Riipinen, I., Komppula, M., Tunved, P., Korhonen, L., Suur-Uski, V., Hirsikko, A., Kurten, T., Kerminen, V.-M., Lihavainen, H., Viisanen, Y., Hansson, H.-C., and Kulmala, M. (2007). Aerosol size distribution measurements at four Nordic field stations: identification, analysis and trajectory analysis of new particle formation bursts. *Tellus Ser. B*, 59(3):350–361.
- Damian, V., Sandu, A., Damian, M., Potra, F., and Carmichael, G. R. (2002). The kinetic preprocessor KPP-a software environment for solving chemical kinetics. *Comput. Chem. Eng.*, 26(11):1567–1579.
- Day, M. C. and Pandis, S. N. (2011). Predicted changes in summertime organic aerosol concentrations due to increased temperatures. *Atmos. Environ.*, 45(36):6546–6556.
- Douwes, J., Thorne, P., Pearce, N., and Heederik, D. (2003). Bioaerosol health effects and exposure assessment: progress and prospects. *Ann. Occup. Hyg.*, 47(3):187–200.
- Draxler, R. R. and Hess, G. D. (1998). An overview of the HYSPLIT_4 modelling system for trajectories, dispersion and deposition. *Aust. Meteor. Mag.*, 47(4):295–308.
- EEA the European Environment Agency (2014). Sulphur dioxide SO₂ emissions (APE 001) - Assessment published Jan 2014. Technical report. <http://www.eea.europa.eu/data-and-maps/indicators/eea-32-sulphur-dioxide-so2-emissions-1/assessment-3>, European Environment Agency (EEA), Copenhagen, Denmark.
- Ehn, M., Petäjä, T., Aufmhoff, H., Aalto, P., Hämeri, K., Arnold, F., Laaksonen, A., and Kulmala, M. (2007). Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid. *Atmos. Chem. Phys.*, 7(1):211–222.

- Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F. (2014). A large source of low-volatility secondary organic aerosol. *Nature*, 506(7489):476–479.
- Eisele, F. and Tanner, D. (1990). Identification of ions in continental air. *J. Geophys. Res. -Atmos*, 95(D12):20539–20550.
- Englund, F. and Nussbaum, R. M. (2000). Monoterpenes in scots pine and norway spruce and their emission during kiln drying. *Holzforschung*, 54(5):449–456.
- Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P. (1995). A global-model of natural volatile organic-compound emissions. *J. Geophys. Res. -Atmos*, 100(D5):8873–8892.
- Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X. (2012). The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. *Geosci. Model Dev.*, 5(6):1471–1492.
- Hakola, H., Hellén, H., Hemmilä, M., Rinne, J., and Kulmala, M. (2012). In situ measurements of volatile organic compounds in a boreal forest. *Atmos. Chem. Phys.*, 12(23):11665–11678.
- Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellen, H., and Keronen, P. (2003). Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.*, 37(12):1623–1634.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J. (2009). The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.*, 9(14):5155–5236.

- Hamill, P., Turco, R., Kiang, C., Toon, O., and Whitten, R. (1982). An analysis of various nucleation mechanisms for sulfate particles in the stratosphere. *J. Aerosol Sci.*, 13(6):561–585.
- Han, X., Zhang, M., Tao, J., Wang, L., Gao, J., Wang, S., and Chai, F. (2013). Modeling aerosol impacts on atmospheric visibility in Beijing with RAMS-CMAQ. *Atmos. Environ.*, 72(0):177–191.
- Hao, L. Q., Romakkaniemi, S., Yli-Pirila, P., Joutsensaari, J., Kortelainen, A., Kroll, J. H., Miettinen, P., Vaattovaara, P., Tiitta, P., Jaatinen, A., Kajos, M. K., Holopainen, J. K., Heijari, J., Rinne, J., Kulmala, M., Worsnop, D. R., Smith, J. N., and Laaksonen, A. (2011). Mass yields of secondary organic aerosols from the oxidation of alpha-pinene and real plant emissions. *Atmos. Chem. Phys.*, 11(4):1367–1378.
- Hari, P. and Kulmala, M. (2005). Station for measuring ecosystem-atmosphere relations (SMEAR II). *Boreal Env. Res.*, 10(5):315–322.
- Haywood, J. and Boucher, O. (2000). Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: A review. *Rev. Geophys.*, 38(4):513–543.
- Heiden, A. C., Kobel, K., Langebartels, C., Schuh-Thomas, G., and Wildt, J. (2003). Emissions of oxygenated volatile organic compounds from plants - part I: Emissions from lipoxygenase activity. *J. Atmos. Chem.*, 45(2):143–172.
- Hirsikko, A., Nieminen, T., Gagné, S., Lehtipalo, K., Manninen, H., Ehn, M., Horrak, U., Kerminen, V.-M., Laakso, L., and McMurry, P. (2011). Atmospheric ions and nucleation: a review of observations. *Atmos. Chem. Phys.*, 11(2):767–798.
- Hoppel, W., Frick, G., Fitzgerald, J., and Larson, R. (1994). Marine boundary layer measurements of new particle formation and the effects nonprecipitating clouds have on aerosol size distribution. *J. Geophys. Res. -Atmos.*, 99(D7):14443–14459.
- IPCC the Intergovernmental Panel on Climate Change (2013). Climate Change 2013: The Physical Science Basis. Technical report. http://www.climatechange2013.org/images/report/WG1AR5_ALL_FINAL.pdf, IPCC secretariat, Geneva, Switzerland.

- Järvinen, E., Virkkula, A., Nieminen, T., Aalto, P. P., Asmi, E., Lanconelli, C., Busetto, M., Lupi, A., Schioppo, R., Vitale, V., Mazzola, M., Petäjä, T., Kerminen, V. M., and Kulmala, M. (2013). Seasonal cycle and modal structure of particle number size distribution at dome c, antarctica. *Atmos. Chem. Phys.*, 13(15):7473–7487.
- Jenkin, M., Wyche, K., Evans, C., Carr, T., Monks, P., Alfarra, M., Barley, M., McFiggans, G., Young, J., and Rickard, A. (2012). Development and chamber evaluation of the MCM v3. 2 degradation scheme for β -caryophyllene. *Atmos. Chem. Phys.*, 12(11):5275–5308.
- Jenkin, M. E., Saunders, S. M., and Pilling, M. J. (1997). The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmos. Environ.*, 31(1):81–104.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J. (2005). Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.*, 5:1053–1123.
- Kerminen, V.-M., Paramonov, M., Anttila, T., Riipinen, I., Fountoukis, C., Korhonen, H., Asmi, E., Laakso, L., Lihavainen, H., and Swietlicki, E. (2012). Cloud condensation nuclei production associated with atmospheric nucleation: a synthesis based on existing literature and new results. *Atmos. Chem. Phys.*, 12(24):12037–12059.
- Kiendler-Scharr, A., Wildt, J., Dal Maso, M., Hohaus, T., Kleist, E., Mentel, T. F., Tillmann, R., Uerlings, R., Schurr, U., and Wahner, A. (2009). New particle formation in forests inhibited by isoprene emissions. *Nature*, 461(7262):381–384.
- Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petaja,

- T., Schnitzhofer, R., Seinfeld, J. H., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M. (2011). Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature*, 476(7361):429–433.
- Köhler, H. (1936). The nucleus in and the growth of hygroscopic droplets. *J. Chem. Soc. Faraday Trans.*, 32:1152–1161.
- Kokkola, H., Yli-Pirilä, P., Vesterinen, M., Korhonen, H., Keskinen, H., Romakkaniemi, S., Hao, L., Kortelainen, A., Joutsensaari, J., and Worsnop, D. (2014). The role of low volatile organics on secondary organic aerosol formation. *Atmos. Chem. Phys.*, 14(3):1689–1700.
- Korhonen, H., Lehtinen, K. E. J., and Kulmala, M. (2004). Multicomponent aerosol dynamics model UHMA: model development and validation. *Atmos. Chem. Phys.*, 4:757–771.
- Kroll, J. H. and Seinfeld, J. H. (2008). Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.*, 42(16):3593–3624.
- Kulmala, M. and Kerminen, V. M. (2008). On the formation and growth of atmospheric nanoparticles. *Atmos. Res.*, 90(2-4):132–150.
- Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., and Rantala, P. (2013a). Direct observations of atmospheric aerosol nucleation. *Science*, 339(6122):943–946.
- Kulmala, M., Lehtinen, K. E. J., and Laaksonen, A. (2006). Cluster activation theory as an explanation of the linear dependence between formation rate of 3nm particles and sulphuric acid concentration. *Atmos. Chem. Phys.*, 6:787–793.
- Kulmala, M., Nieminen, T., Chellapermal, R., Makkonen, R., Bäck, J., and Kerminen, V.-M. (2013b). *Climate Feedbacks Linking the Increasing Atmospheric CO₂ Concentration, BVOC Emissions, Aerosols and Clouds in Forest Ecosystems*, volume 5 of *Tree Physiology*, chapter 17, pages 489–508. Springer Netherlands.
- Kulmala, M., Nieminen, T., Nikandrova, A., Lehtipalo, K., Manninen, H. E., Kajos, M. K., Kolari, P., Lauri, A., Petäjä, T., Krejci, R., Hansson, H.-C., Swietlicki, E.,

- Lindroth, A., Christensen, T. R., Arneth, A., Hari, P., Bäck, J., Vesala, T., and Kerminen, V.-M. (2014a). CO₂-induced terrestrial climate feedback mechanism: From carbon sink to aerosol source and back. *Boreal Env. Res.*, 19 (suppl. B):122–131.
- Kulmala, M., Petäjä, T., Ehn, M., Thornton, J., Sipilä, M., Worsnop, D., and Kerminen, V.-M. (2014b). Chemistry of Atmospheric Nucleation: On the Recent Advances on Precursor Characterization and Atmospheric Cluster Composition in Connection with Atmospheric New Particle Formation. *Annu. Rev. Phys. Chem.*, 65:21–37.
- Kulmala, M., Pirjola, U., and Makela, J. M. (2000). Stable sulphate clusters as a source of new atmospheric particles. *Nature*, 404(6773):66–69.
- Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H. E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., and Kerminen, V. M. (2007). Toward direct measurement of atmospheric nucleation. *Science*, 318(5847):89–92.
- Kulmala, M., Suni, T., Lehtinen, K. E. J., Dal Maso, M., Boy, M., Reissell, A., Rannik, U., Aalto, P., Keronen, P., Hakola, H., Back, J. B., Hoffmann, T., Vesala, T., and Hari, P. (2004a). A new feedback mechanism linking forests, aerosols, and climate. *Atmos. Chem. Phys.*, 4:557–562.
- Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W., and McMurry, P. H. (2004b). Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.*, 35:143–176.
- Kyrö, E.-M., Kerminen, V.-M., Virkkula, A., Maso, M. D., Parshintsev, J., Ruiz-Jimenez, J., Forsström, L., Manninen, H., Riekkola, M.-L., Heinonen, P., and Kulmala, M. (2013). Antarctic new particle formation from continental biogenic precursors. *Atmos. Chem. Phys.*, 13(7):3527–3546.
- Laaksonen, A., Kulmala, M., O’Dowd, C., Joutsensaari, J., Vaattovaara, P., Mikkonen, S., Lehtinen, K., Sogacheva, L., Maso, M. D., and Aalto, P. (2008). The role of VOC oxidation products in continental new particle formation. *Atmos. Chem. Phys.*, 8(10):2657–2665.
- Lappalainen, H. K., Sevanto, S., Back, J., Ruuskanen, T. M., Kolari, P., Taipale, R., Rinne, J., Kulmala, M., and Hari, P. (2009). Day-time concentrations of biogenic

- volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors. *Atmos. Chem. Phys.*, 9(15):5447–5459.
- Leaitch, W. R., Macdonald, A. M., Brickell, P. C., Liggio, J., Sjostedt, S. J., Vlasenko, A., Bottenheim, J. W., Huang, L., Li, S. M., Liu, P. S. K., Toom-Sauntry, D., Hayden, K. A., Sharma, S., Shantz, N. C., Wiebe, H. A., Zhang, W. D., Abbatt, J. P. D., Slowik, J. G., Chang, R. Y. W., Russell, L. M., Schwartz, R. E., Takahama, S., Jayne, J. T., and Ng, N. L. (2011). Temperature response of the submicron organic aerosol from temperate forests. *Atmos. Environ.*, 45(37):6696–6704.
- Lindinger, W., Hansel, A., and Jordan, A. (1998). On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (ptr-ms) - medical applications, food control and environmental research. *Int. J. Mass Spectrom.*, 173(3):191–241.
- Matsunaga, A. and Ziemann, P. J. (2010). Gas-wall partitioning of organic compounds in a Teflon film chamber and potential effects on reaction product and aerosol yield measurements. *Aerosol Sci. Tech.*, 44(10):881–892.
- Mauldin III, R., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurtén, T., Stratmann, F., Kerminen, V.-M., and Kulmala, M. (2012). A new atmospherically relevant oxidant of sulphur dioxide. *Nature*, 488(7410):193–196.
- Mentel, T. F., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Dal Maso, M., Fisseha, R., Hohaus, T., Spahn, H., Uerlings, R., Wegener, R., Griffiths, P. T., Dinar, E., Rudich, Y., and Wahner, A. (2009). Photochemical production of aerosols from real plant emissions. *Atmos. Chem. Phys.*, 9(13):4387–4406.
- Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C., and Seinfeld, J. H. (2007). Secondary aerosol formation from atmospheric reactions of aliphatic amines. *Atmos. Chem. Phys.*, 7(9):2313–2337.
- Oderbolz, D., Aksoyoglu, S., Keller, J., Barmpadimos, I., Steinbrecher, R., Skjøth, C. A., Plaß-Dülmer, C., and Prévôt, A. (2013). A comprehensive emission inventory of biogenic volatile organic compounds in europe: improved seasonality and land-cover. *Atmos. Chem. Phys.*, 13(4):1689–1712.

- O'Dowd, C. D., Hämeri, K., Mäkelä, J. M., Pirjola, L., Kulmala, M., Jennings, S. G., Berresheim, H., Hansson, H.-C., de Leeuw, G., and Kunz, G. J. (2002). A dedicated study of new particle formation and fate in the coastal environment (PARFORCE): Overview of objectives and achievements. *J. Geophys. Res. -Atmos.*, 107(D19):PAR 1–1–PAR 1–16.
- Paasonen, P., Asmi, A., Petäjä, T., Kajos, M. K., Aijala, M., Junninen, H., Holst, T., Abbatt, J. P. D., Arneth, A., Birmili, W., van der Gon, H. D., Hamed, A., Hoffer, A., Laakso, L., Laaksonen, A., Richard Leaitch, W., Plass-Dulmer, C., Pryor, S. C., Raisanen, P., Swietlicki, E., Wiedensohler, A., Worsnop, D. R., Kerminen, V.-M., and Kulmala, M. (2013). Warming-induced increase in aerosol number concentration likely to moderate climate change. *Nature Geosci.*, 6(6):438–442.
- Paasonen, P., Nieminen, T., Asmi, E., Manninen, H., Petäjä, T., Plass-Dülmer, C., Flentje, H., Birmili, W., Wiedensohler, A., and Horrak, U. (2010). On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation. *Atmos. Chem. Phys.*, 10(22):11223–11242.
- Park, S. H., Kim, H. O., Han, Y. T., Kwon, S. B., and Lee, K. W. (2001). Wall loss rate of polydispersed aerosols. *Aerosol Sci. Tech.*, 35(3):710–717.
- Petäjä, T., Mauldin III, R., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T., and Kulmala, M. (2009). Sulfuric acid and OH concentrations in a boreal forest site. *Atmos. Chem. Phys.*, 9(19):7435–7448.
- Pope, C. A., Burnett, R. T., Thurston, G. D., Thun, M. J., Calle, E. E., Krewski, D., and Godleski, J. J. (2004). Cardiovascular mortality and long-term exposure to particulate air pollution epidemiological evidence of general pathophysiological pathways of disease. *Circulation*, 109(1):71–77.
- Raatikainen, T., Vaattovaara, P., Tiitta, P., Miettinen, P., Rautiainen, J., Ehn, M., Kulmala, M., Laaksonen, A., and Worsnop, D. R. (2010). Physicochemical properties and origin of organic groups detected in boreal forest using an aerosol mass spectrometer. *Atmos. Chem. Phys.*, 10(4):2063–2077.
- Raes, F., Janssens, A., and Van Dingenen, R. (1986). The role of ion-induced aerosol formation in the lower atmosphere. *J. Aerosol Sci.*, 17(3):466–470.

- Riccobono, F., Schobesberger, S., Scott, C. E., Dommen, J., Ortega, I. K., Rondo, L., Almeida, J. a., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Downard, A., Dunne, E. M., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Hansel, A., Junninen, H., Kajos, M., Keskinen, H., Kupc, A., Kürten, A., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Nieminen, T., Onnela, A., Petäjä, T., Praplan, A. P., Santos, F. D., Schallhart, S., Seinfeld, J. H., Sipilä, M., Spracklen, D. V., Stozhkov, Y., Stratmann, F., Tomé, A., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Wimmer, D., Carslaw, K. S., Curtius, J., Donahue, N. M., Kirkby, J., Kulmala, M., Worsnop, D. R., and Baltensperger, U. (2014). Oxidation products of biogenic emissions contribute to nucleation of atmospheric particles. *Science*, 344(6185):717–721.
- Riipinen, I., Sihto, S. L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinila, K., Kerminen, V. M., Laaksonen, A., and Lehtinen, K. E. J. (2007). Connections between atmospheric sulphuric acid and new particle formation during QUEST III-IV campaigns in Heidelberg and Hyytiälä. *Atmos. Chem. Phys.*, 7(8):1899–1914.
- Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T., Worsnop, D. R., Kulmala, M., and Donahue, N. M. (2012). The contribution of organics to atmospheric nanoparticle growth. *Nature Geosci.*, 5(7):453–458.
- Roberts, G. and Nenes, A. (2005). A continuous-flow streamwise thermal-gradient ccm chamber for atmospheric measurements. *Aerosol Sci. Technol.*, 39(3):206–221.
- Roldin, P., Eriksson, A. C., Nordin, E. Z., Hermansson, E., Mogensen, D., Rusanen, A., Boy, M., Swietlicki, E., Svenningsson, B., Zelenyuk, A., and Pagels, J. (2014). Modelling non-equilibrium secondary organic aerosol formation and evaporation with the aerosol dynamics, gas- and particle-phase chemistry kinetic multilayer model ADCHAM. *Atmos. Chem. Phys.*, 14(15):7953–7993.
- Schade, G. W. and Goldstein, A. H. (2003). Increase of monoterpene emissions from a pine plantation as a result of mechanical disturbances. *Geophys. Res. Lett.*, 30(7).
- Schimang, R., Folkers, A., Kleffmann, J., Kleist, E., Miebach, M., and Wildt, J. (2006). Uptake of gaseous nitrous acid (HONO) by several plant species. *Atmos. Environ.*, 40(7):1324–1335.

- Schobesberger, S., Junninen, H., Bianchi, F., Lönn, G., Ehn, M., Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I. K., Franchin, A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J., Almeida, J., Amorim, A., Breitenlechner, M., Downard, A. J., Dunne, E. M., Flagan, R. C., Kajos, M., Keskinen, H., Kirkby, J., Kupc, A., Kürten, A., Kurtén, T., Laaksonen, A., Mathot, S., Onnela, A., Praplan, A. P., Rondo, L., Santos, F. D., Schallhart, S., Schnitzhofer, R., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Vehkamäki, H., Wimmer, D., Baltensperger, U., Carslaw, K. S., Curtius, J., Hansel, A., Petäjä, T., Kulmala, M., Donahue, N. M., and Worsnop, D. R. (2013). Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules. *Proc. Nat. Acad. Sc. USA*, 110(43):17223–17228.
- Seinfeld, J. H. and Pandis, S. N. (2012). *Atmospheric Chemistry and Physics: from air pollution to climate change*. John Wiley & Sons.
- Shen, X. J., Sun, J. Y., Zhang, Y. M., Wehner, B., Nowak, A., Tuch, T., Zhang, X. C., Wang, T. T., Zhou, H. G., Zhang, X. L., Dong, F., Birmili, W., and Wiedensohler, A. (2011). First long-term study of particle number size distributions and new particle formation events of regional aerosol in the North China Plain. *Atmos. Chem. Phys.*, 11(4):1565–1580.
- Sihto, S. L., Kulmala, M., Kerminen, V. M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J. (2006). Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms. *Atmos. Chem. Phys.*, 6:4079–4091.
- Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, Roy L., I., Hyvarinen, A.-P., Lihavainen, H., and Kulmala, M. (2010). The role of sulfuric acid in atmospheric nucleation. *Science*, 327(5970):1243–1246.
- Spracklen, D., Jimenez, J., Carslaw, K., Worsnop, D., Evans, M., Mann, G., Zhang, Q., Canagaratna, M., Allan, J., and Coe, H. (2011). Aerosol mass spectrometer constraint on the global secondary organic aerosol budget. *Atmos. Chem. Phys.*, 11(23):12109–12136.
- Steinbrecher, R., Hauff, K., Rössler, J., Dürr, M., and Seufert, G. (1999). Monoterpene emission from soils in orange plantations of the valencian citrus belt, Spain. *Phys. Chem. Earth Pt. B*, 24(6):695–698.

- Stevens, B. (2013). Aerosols: Uncertain then, irrelevant now. *Nature*, 503(7474):47–48.
- Stier, P., Seinfeld, J. H., Kinne, S., and Boucher, O. (2007). Aerosol absorption and radiative forcing. *Atmos. Chem. Phys.*, 7:5237–5261.
- Sun, Q., Hong, X., and Wold, L. E. (2010). Cardiovascular effects of ambient particulate air pollution exposure. *Circulation*, 121(25):2755–2765.
- Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H. (2006). Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. *J. Phys. Chem. A*, 110(31):9665–9690.
- Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., and Kulmala, M. (2008). Technical note: Quantitative long-term measurements of VOC concentrations by PTR-MS - measurement, calibration, and volume mixing ratio calculation methods. *Atmos. Chem. Phys.*, 8(22):6681–6698.
- Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., and Kulmala, M. (2005). Temperature and light dependence of the VOC emissions of Scots pine. *Atmos. Chem. Phys.*, 5(4):989–998.
- Topping, D., McFiggans, G., Kiss, G., Varga, Z., Facchini, M., Decesari, S., and Mircea, M. (2007). Surface tensions of multi-component mixed inorganic/organic aqueous systems of atmospheric significance: measurements, model predictions and importance for cloud activation predictions. *Atmos. Chem. Phys.*, 7(9):2371–2398.
- Tunved, P., Hansson, H. C., Kerminen, V. M., Strom, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M. (2006). High natural aerosol loading over boreal forests. *Science*, 312(5771):261–263.
- Tunved, P., Stroem, J., Kulmala, M., Kerminen, V. M., Dal Maso, M., Svenningsson, B., Lunder, C., and Hansson, H. C. (2008). The natural aerosol over northern europe and its relation to anthropogenic emissions - implications of important climate feedbacks. *Tellus Ser. B*, 60(4):473–484.
- Väänänen, R., Kyrö, E.-M., Nieminen, T., Kivekäs, N., Junninen, H., Virkkula, A., Dal Maso, M., Lihavainen, H., Viisanen, Y., Svenningsson, B., Holst, T., Arneth, A., Aalto, P. P., Kulmala, M., and Kerminen, V.-M. (2013). Analysis of particle

- size distribution changes between three measurement sites in northern scandinavia. *Atmos. Chem. Phys.*, 13(23):11887–11903.
- VanReken, T. M., Greenberg, J. P., Harley, P. C., Guenther, A. B., and Smith, J. N. (2006). Direct measurement of particle formation and growth from the oxidation of biogenic emissions. *Atmos. Chem. Phys.*, 6:4403–4413.
- Vestenius, M., Hellén, H., Levula, J., Kuronen, P., Helminen, K., Nieminen, T., Kulmala, M., and Hakola, H. (2014). Acidic reaction products of monoterpenes and sesquiterpenes in atmospheric fine particles in a boreal forest. *Atmos. Chem. Phys.*, 14(15):7883–7893.
- Virkkula, A., Van Dingenen, R., Raes, F., and Hjorth, J. (1999). Hygroscopic properties of aerosol formed by oxidation of limonene, α -pinene, and β -pinene. *J. Geophys. Res.-Atmos.*, 104(D3):3569–3579.
- Wallace, P. J. (2001). Volcanic SO₂ emissions and the abundance and distribution of exsolved gas in magma bodies. *J. Volcanol. Geotherm. Res.*, 108(1):85–106.
- Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A. (1996). Measured atmospheric new particle formation rates: Implications for nucleation mechanisms. *Chem. Eng. Commun.*, 151:53–64.
- Yu, F. Q. and Turco, R. P. (2000). Ultrafine aerosol formation via ion-mediated nucleation. *Geophys. Res. Lett.*, 27(6):883–886.
- Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H. (2014). Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol. *Proc. Nat. Acad. Sc. USA*, 111(16):5802–5807.
- Zheng, J., Hu, M., Zhang, R., Yue, D., Wang, Z., Guo, S., Li, X., Bohn, B., Shao, M., and He, L. (2011). Measurements of gaseous H₂SO₄ by AP-ID-CIMS during CAREBeijing 2008 campaign. *Atmos. Chem. Phys.*, 11(15):7755–7765.