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EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM BOREAL HUMIC LAKES

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Keywords: VOCs, BOREAL LAKE, CLIMATE CHANGE.

INTRODUCTION

Biological sources of VOCs in aquatic ecosystems are related to algal and microbial functions, which have been reported to produce significant quantities of volatile compounds, e.g. dimethyl sulphide, isoprene and monoterpenes (Colomb et al., 2008; Yassaa et al., 2008) especially during the algal bloom periods. Oceans have proven to be significant sources of aerosol precursor gases, but in inland lakes also algae and bacteria may produce VOCs in quantities comparable to those of terrestrial soil and forest floor vegetation (Bäck et al., manuscript in preparation). The diurnal pattern observed in freshwater VOC emissions suggests a significant contribution of biological (both bacterial and algae) processes on the production of VOCs.

Aquatic VOC emissions have mostly been measured during the ice-free period when the biological activity is greatest. However, the ice cover does not inhibit bacterial metabolism, which is independent on light. Since also algal photosynthesis begins already below the ice cover after snow has disappeared and saturates at very low PAR levels (Tulonen et al., 1994; Ojala, pers. comm.), it is anticipated that biologically produced VOCs could accumulate beneath the ice cover, and released to the air during the ice melt period. In freezing marine ecosystems the VOCs may also be accumulated in the brine pockets. In this project we conducted springtime VOC measurements on boreal lakes hypothesizing that:

1) ice cover does not restrain VOC production in boreal lakes, and
2) melting of ice may lead to a burst of accumulated VOCs from the top layers of the water column

METHODS

The springtime emissions of terpenoids were measured from two boreal lakes: on the Lake Kuivajärvi, in southern Finland and on Lake Erssjön, in southern Sweden (Figure 1). Measurements were conducted with floating flow-through chambers and the samples were taken from air entering and leaving the enclosure to adsorbent tubes (Tenax TA-Carbopack B). Samplings were performed with three campaigns, starting at the time of ice melt. Earlier at the winter, background samples were taken from a chamber placed above a small hole in the ice cover. Terpenoid analyses from adsorbent tubes were performed at the Finnish Meteorological Institute with thermodesorption-gas chromatograph-mass spectrometer (TD-GC-MS).
In addition to the VOC emission measurements, terpenoid and short-chained hydrocarbon concentrations were measured parallel on the Lake Kuivajärvi with on-line TD-GC-MS, and these measurements are still on-going. The concentrations were measured about 50 cm above water surface and the sampling inlet was coupled with 3D ultrasonic anemometer.

The VOC emission measurements were combined with those of air temperature, solar radiation, chlorophyll, and phytoplankton populations. Phytoplankton samples will be analysed later in the laboratory under microscope as well as phytobiomass using chlorophyll determination with a spectrophotometer. At the Lake Kuivajärvi, measurement raft provides plenty of data about physical parameters and gas concentrations ($O_2$, $CO_2$, $CH_4$) in the lake and gas fluxes from the lake. In both the lakes, water balance as well as carbon input and output were continuously monitored.

RESULTS AND CONCLUSIONS

The preliminary data shows measurable terpenoid emissions from boreal lakes and the emissions consist on several mono- and sesquiterpenes. However, the absolute springtime emissions seem to be quite low in both the lakes, and a burst in the emission during/after ice melt was not observable. The emissions seem to increase during the spring with higher temperatures. The data on terpenoid and short-chained carbohydrate concentrations from the Lake Kuivajärvi are not yet available.

The three most abundant compounds in aquatic terpenoid emissions were monoterpenes \( \alpha \)-pinene, \( \Delta^3 \)-carene and \( \beta \)-pinene, same compounds that are abundant also in VOC fluxes from boreal forest floor (Aaltonen et al., 2011). Several sesquiterpenes (most abundantly longifolene) were also seen in the emissions, although generally their emission rates were very low. The oxygenated terpenoids linalool and bornyl acetate were emitted in notable amounts.

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EXAMINING HETEROGENEITY IN THE BOREAL PEATLAND-ATMOSPHERE FLUX SOURCES

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Keywords: wetlands, microsites, carbon cycle, energy cycle.

INTRODUCTION

Boreal peatlands are known to be a massive storage of soil carbon, making up to about 20\% of the world terrestrial carbon reserves. The carbon storage in peatlands has played a crucial role in the climate development since the last glacial period. Nowadays, however, the changing climate has been exerting a pressure on boreal peatlands under which their carbon reserves are becoming unstable. Massive evidence suggests that the expected climate shifts may destabilize the peatlands enough for the major fraction of their organic carbon to be emitted into the atmosphere in the form of greenhouse gases, mainly as CO\textsubscript{2} and CH\textsubscript{4}. At the same time, the peat accumulation zone may progress northwards as the arctic climate changes (Charman \textit{et al.}, 2013).

Besides that, however, peatlands have the potential to alter the climate through the energy exchange with the atmosphere. This process bears importance on many scales. At the scale of 1 to 10 m\textsuperscript{2}, it is responsible for the heating of peat, which directly controls the production of GHG; at the scale of 10 to 100 km\textsuperscript{2}, the Bowen ratio largely determines the local and regional climate. On an even larger scale, the conversion between the open peatlands and forested areas, occurring both naturally and through management, feeds back to the global climate.

Specific features of boreal climate have led the peatlands to develop distinctive microtopography with the associated differences in the vegetation communities, peat characteristics and hydraulics (Bridgham \textit{et al.}, 1996). Those differences have been shown to create steep gradients in the mass and energy exchange in wetlands. This implies that ecosystem-scale exchange processes at wetlands cannot be modelled correctly without account of the differences in microsite dynamics.

Siikaneva, the biggest wetland to remain in its natural state in Southern Finland, is a perfect polygon for the examination of the peatland microsite heterogeneity. This important aspect of the wetland biogeochemistry is addressed at the bog part of the wetland, the site known as Siikaneva-2.

METHODS AND AIMS

The bog area of Siikaneva has been the site of various multi-scale experiments brought out by the collaboration of the University of Helsinki, University if Eastern Finland and the Finnish Meteorological Institute. The work that has been brought out at the site during the three field seasons of 2011-2013 and is to be continued includes:

1) Eddy-covariance measurements. The EC setup in Siikaneva-2 provides the ecosystem-scale estimates of CO\textsubscript{2}, CH\textsubscript{4}, sensible and latent heat fluxes. The the EC-derived wetland-atmosphere exchange rates provide twofold information that may be hard to interpret because of the source heterogeneity. In the first few tens of meters near the EC mast, the primary source area of the turbulent fluxes may have the size comparable with the sizes of individual microsites. Farther away, the microsite mosaic is less important, since the turbulent fluxes effectively become spatially averaged at larger distances from the EC sensor.

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2) Manual chamber measurements. The chamber measurements are performed at 6 microsites; each microsite is sampled 3 times for better representativeness. The microforms currently measured are: high hummock, hummock, high lawn, lawn, hollow and mud bottom. Additionally, floating chambers are used to estimate the ebullition flux from mud bottoms / pond surfaces.

3) Gas concentration sampling. Dissolved gas collection points are equipped with the tubes reaching down to 2m depths in all representative microsites. Through these measurements, we hope to obtain new evidence of the greenhouse gas production across the bog microtopography gradient.

4) Vegetation sampling. Examination of the vegetation composition has been brought out within the 99% contribution area of EC fluxes (200m radius around the EC mast). A total of 354 plots have been sampled, with the additional sampling in the maximum EC contribution zone to follow. Derived quantities include leaf area index, biomass and species composition.

5) LIDAR and aerial photography. Completed in spring 2013, these remote sensing campaign has provided a high-resolution view of the area around the site, which will be used to construct the source mosaic map, in coordination with the vegetation map.

6) Net radiation and temperature monitoring. 4 pairs of \( R_{\text{net}} \) sensors and \( T_{\text{peat}} \) profiles (down to 0.3m depth) have been installed at representative microsites, since we expect different with respect to the net radiation flux and the soil heat conduction. These are tightly linked with e.g. microsite-specific surface cover, peat structure and water content.

7) Collection of peat cores and peat depth measurements along transects. Done throughout the extent of the wetland, these data will help reconstruct the peatland development in the past and may be used to forecast the state of the wetland under future climate conditions.

Figure 1. Organization of measurements and campaigns at the Siikaneva-2 site. Due to the larger spatial scale of the work, the peat cores are not included. Vegetation sampling points are uniformly distributed over the footprint zone.
Our ultimate purpose is to draw clear distinction between the responses of different microsites to the main environmental drivers such as interannual weather fluctuations or peatland management, and their individual contributions to the local and regional carbon and energy balances.

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The effect of cloudiness on new particle formation: investigation of radiation levels

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Keywords: Relative radiation intensity, New Particle Formation, Cloudiness, Hyytiälä.

INTRODUCTION

Atmospheric New particle formation events (NPF), i.e. nucleation and the growth of the newly formed particles have been well documented in many different environments all around the world (Kulmala et al., 2004 and references therein). Many studies have been done to find out the important variables causing and preventing the NPF events. Hyvönen et al. (2005) showed that low relative humidity and condensation sink are the key factors for occurrence of a NPF event in Hyytiälä, Finland. Boy and Kulmala (2002), on the other hand, suggested that low atmosphere water content, low condensation sink, and high solar radiation, in particular the UV-A component, create favorable circumstances for NPF. They showed that appearance of clouds during the events did sometimes stop the nucleation, and sometimes nucleation continued after the disappearance of clouds. Moreover, they concluded that the radiation level required for the appearance of the smallest detectable 3 nm particles is more than one third of daily maximum radiation and that nucleation stops when the radiation decreases below the same value. The importance of solar radiation as a driver of new particle formation has been firmly confirmed in the literature. However, seasonal cloud effects on NPF-events and radiation levels during nucleation have not been systematically investigated. In this research, we study these cloud effects on NPF using a relative radiation intensity parameter as an indicator of cloudiness level.

SITE DESCRIPTION

This research has been done using data obtained at the SMEAR II station characterized by boreal coniferous forest, located in Hyytiälä (61°51’ N, 24°17’ E, 181 m asl), Southern Finland. The station is affected by pollution coming from Tampere city (60 km) and also the buildings (0.5 km) near to instruments (Boy and Kulmula, 2002). The particle size distribution measurements in diameter size ranges 3-500 nm is carried out by Twin Differential Mobility Particle Sizer (TDMPS) system.

METHODS

We calculated the relative radiation intensity (hereafter ratio) defined as the ratio of measured global-radiation I (w/m2) at a given time divided by the clear-sky global radiation Imax (w/m2) at the same time for all days during 2002-2012. However, we only analysed the ratio I/Imax for the duration between nucleation start and end times (i.e. the times when 3nm particle production starts and ends, respectively - hereafter 3nm-time-window) for NPF event days, and from one hour after sunrise until noon for Non-events and undefined days. The 3nm-time-window was defined visually from the so called banana plots. The global radiation (I) data are actual measurement data collected from SMEAR II station in half-hour average resolution during 2002-2012. The Imax data are modelled clear sky data downloaded from the AERONET website (http://aeronet.gsfc.nasa.gov/). We classified the NPF-event days as “quantifiable” and “non-quantifiable” according the criterion introduced by Dal Maso et al (2005) which is whether the event is homogeneous enough to quantify the basic characteristics such as formation rate and growth rate.
or not. We left out the days where the DMPS instrument had broken resulting in No-data days and Bad-
days of size distribution. Therefore, our data pool consists of event, non-event and undefined days, the
latter being days during which the evolution of the size distribution is too unclear for definitive
determination of whether or not NPF has been occurring.

RESULTS AND DISCUSSION

Statistical analysis:

Figure 1 shows the fraction (%) of days (Event+Non-event+undefined) which are event or non-event in a
given range of the ratio $I/I_{\text{max}}$ provided that values of $I/I_{\text{max}}$ have stayed in the given range for a continuous
time of at least one hour. The width of the interval (0.2) and the spacing (0.05) are set so as to preserve as
much as possible of the data. As can be seen from the figure, the higher (lower) the $I/I_{\text{max}}$ values, the more
(less) event (non-event) days, so that 55% of days are NPF-event, 10 % non-event and the rest are
undefined in highest range 0.8-1. Note that undefined days and different time windows for events (3nm
duration) and non-events (one hour after sunrise until noon) in which $I/I_{\text{max}}$ is analysed, can bias the
fraction values of figure 1. Few event days having low ratio ranges (i.e. cloudy sky) can be seen. For
example about 10 % of days in range 0.3-0.5 are event days. This means that cloudy sky condition could
be dominated either sometime within or during whole 3nm-time-window of event. In addition, Figure 1
shows that non-events can also occur despite of high relative radiation intensity radiation, meaning that
clear sky is not a sufficient condition for a nucleation event occurrence. A surprising result is that the
percentage of both event and non-event days seem to plateau in the $I/I_{\text{max}}$ range 0.55-0.85.

![Figure 1](image)

Figure 1. Event and Non-event fraction (%) in different ratio $I/I_{\text{max}}$ ranges in Hyytiälä during period 2002-2012.

To investigate seasonal cloud effects on NPF-events, the same fraction as figure 1 has been extracted but
for different seasons separately (see Figure 2). The fraction of event days in the $I/I_{\text{max}}$ range 0.8-1 is 50%,
73%, 33% and 61% in winter, spring, summer and autumn respectively. For non-event days, the
corresponding percentages are 20%, 4%, 19% and 8%. This means that event occurrence at clear sky
conditions is much more probable in the other seasons than summer. The same holds for the statistics in
the other high $I/I_{\text{max}}$ ranges 0.75-0.95 and 0.7-0.9. Generally speaking, an increasing trend of event fraction
values with increasing ratio ranges can be seen in all seasons. The plateaus seen in Fig. 1 at the $I/I_{\text{max}}$
ranges 0.55-0.85 are clearly mostly caused by the springtime data. However, the actual reason for the
plateaus is unknown at the present.
Investigation of anomalous days:

NPF event days in which clouds are present during the whole or a substantial part of the 3nm-time-window have been considered as anomalous days. We found about 130 event days in Hyytiälä in which cloudy conditions ($I/I_{\text{max}} < 0.5$) occurred during a substantial time (i.e. at least during one hour) within the 3nm-time-window. We have looked into the auxiliary parameters including Condensation Sink (CS), Relative Humidity (RH), SO$_2$, and temperature to get insight into atmospheric conditions which could favour NPF despite cloudiness. The results show that in most of the mentioned days (about 100 out of 134) the $I/I_{\text{max}}$ values have been higher than 0.5 before appearance of cloud ($I/I_{\text{max}} < 0.5$). The anomalous event days can be categorized to 3 types as follows:

Type 1: Event days with initially clear sky, followed by appearance of clouds has for a while. Appearance of clouds has mostly stopped the generation of 3 nm particles (e.g. 24-Apr-2003, 26 Apr 2004). Type 1 anomalous events are characterized by low condensation sink and low relative humidity as the parameters favouring the NPF.

Type 2: A few event days (about 10 days) in which clouds are present during the whole 3nm-time-window. All of these events are weak (i.e. non-quantifiable). Figure 3 (bottom-left) shows an example of this type of event on 6 Oct 2002. The CS values are low, however, the relative humidity is rapidly increasing during the 3nm-time-window.

Type 3: The event days which start under cloudy conditions: Figure 3 (Top-right) shows a clear event day on 8 Apr 2003 in which clouds are present at the start of the event and for about two hours subsequently, after which the sky clears for the rest of the time window. As can be seen condensation sink is very low during the cloudy hours.
Figure 3. Two anomalous events on 8 April 2003 (Top) with appearance of cloud at start time of event and a weak event on 6 October 2002 (bottom) with appearance of clouds during whole 3nm-time-window, along with their bananas (Bottom).

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REFERENCES


THE INTERPLAY OF LOCAL AND MESOSCALE FACTORS ON THE BOUNDARY LAYER STRUCTURE IN SUMMER AND WINTER AT STATION NORD

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Abstract

We analyse data from measurements and mesoscale meteorological modelling for periods in summer 2011 and winter 2011/2012 to elucidate the boundary-layer features at Station Nord situated in Northern Greenland (81.6N, 16.7W). A major challenge for modelling is to connect local-scale observations with larger scales modelling of the atmosphere. In particular, in summer, bare soil in the vicinity of the station may not be present in the global boundary and surface conditions. Thus, in summer the deviations of modeled from measured values of temperature and humidity near the surface are larger compared to winter. We found that the underestimation of temperature near the ground is larger at clear sky compared to cloudy conditions; and the underestimation reached up to height 1-1.5 km at clear sky and up to the first 100 m for the cloudy days. The measured wind speed profiles showed high variability, while the modeled were smoothed. During summer the modeled wind speed was close to or larger than the measured without clear indication for the role of clouds. In winter, the over-estimation of wind speed was more pronounced.

Mesoscale modelling results

Mesoscale modelling was performed with the Weather Research Forecasting model (with ARW core) WRF, v.3.3.1 (Skamarock et al, 2008). The domain and physics used for the simulations are shown in Figure 1. WRF was initialized with the US National Center for Environmental Prediction Global Analyses data (FNL), with space resolution 1x1 degree and time resolution of 6 hours. WRF was run with two-way nesting on 3 domains with horizontal grid resolution 36, 12, and 4 km, on 26 vertical levels up to 50 hPa (13 of them are below 2000 m). Land use categories of USGS 24-category data were used. The snow free surroundings of the Station Nord in summer are likely not accounted for in the surface conditions and poorly resolved with resolution of 4 km. WRF model temperature profiles are in general close to the observed temperature profiles. The model temperature near the ground is lower in summer with bigger difference at clear sky compared to cloudy conditions; and is closer to measurements in winter. The temperature under estimation reaches height of 1-1.5 km in clear skies and is within the first 100 m for the cloudy days, Figure 2 (upper panels). The measured wind speed profiles show high variability, while the modeled are smoothed; the wind modeled speed near the ground was close to or larger than the measured one without clear indication for the role of clouds. Larger discrepancies were found in winter, compared to summer, Figure 2 (lower panels).
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<tr>
<td>Mycrophysics</td>
<td>8 (D3) = Thompson graupel; 4 (D1&amp;D2)=WSM 5-class</td>
</tr>
<tr>
<td>Longwave radiation</td>
<td>1 = RRTM</td>
</tr>
<tr>
<td>Shortwave radiation</td>
<td>2 = Goddard</td>
</tr>
<tr>
<td>Surface layer</td>
<td>2 = Eta similarity</td>
</tr>
<tr>
<td>Land surface</td>
<td>Noah LSM</td>
</tr>
<tr>
<td>ABL</td>
<td>2 = Mellor-Yamada-Janjic</td>
</tr>
<tr>
<td>Cumulus parametrization</td>
<td>5 = New Grell scheme (D1&amp;D2)</td>
</tr>
</tbody>
</table>

**Figure 1.** Model domains and physics options used.

**Figure 2.** Comparison of modeled and measured profiles

**Acknowledgements**

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**References**

Radiative forcing and global temperature change of future Arctic shipping

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Keywords: Aerosols, radiative forcing, Arctic climate

INTRODUCTION

The melting of sea ice in the Arctic opens up for new shipping routes between Europe and Asia. As this route is considerably shorter than the traditional route through the Suez canal, there is a potential for reduced fuel use and thus reduced CO2 emissions by using the northern sea route. However, shipping leads to emissions of non-CO2 components that also have a climate impact. The main components are NOx, SO2 and black carbon aerosols (BC). NOx leads to formation of ozone and enhancement of OH which increases the oxidation capacity of the atmosphere (and thus reduced methane concentrations and enhanced SO2 oxidation rates) and possibly enhanced levels of nitrate aerosols. Ozone and methane are both greenhouse gases, while nitrate aerosols are primarily scattering, so emissions of NOx have both warming and cooling effects. The SO2 emissions lead to enhanced levels of sulphate aerosols which cool the climate through scattering of solar radiation. The BC aerosols absorb solar radiation either in the atmosphere (the direct effect) or after the aerosols have been deposited on the snow (snow albedo effect). The magnitude of the radiative forcing all these non-CO2 effects are determined by short-lived components and by the physical conditions where the emissions occur. Thus, the net climate impact of the two shipping routes may be quite different than the CO2-only effect.

METHODS

In this study we use future predictions of emissions from bulk carriers developed by the Norwegian Veritas, taking into account projected sea ice cover in 2030 and 2050. (www.dnv.com/binaries/shipping%20across%20the%20arctic%20ocean%20position%20paper_tcm4-434419.pdf). Equal amounts of cargo are assumed to be transported each of the two routes. We use these emission estimates as input to our global CTM, OsloCTM2 (Dalsøren et al., 2013 and references therin) to calculate the impact on all major non-CO2 climate compounds (ozone, methane, sulphate, nitrate, OC and BC aerosols). Based on these calculated concentration fields the radiative forcings are calculated using a radiative transfer model (Myhre et al., 2007). The impact on global CO2 concentrations are calculated using an impulse response function from Joos et al. (2013), and the corresponding radiative forcing is estimated using the standard IPCC formula (IPCC, 2001).

The climate impacts of the SLCE and CO2 have very different time constants. Thus, the net difference between the two routes depends on for how long the emissions are sustained. To analyse this the radiative forcings are used as input to a simple analytical climate model (Berntsen and Fuglestvedt, 2008) and the impacts on global mean temperatures of sustained ship transport through the two routes are estimated.

CONCLUSIONS

Below are some preliminary results from the simulations. Figure 1 shows the calculated impacts on burdens of sulphate and BC aerosols for emissions along the two routes. The reduction in the sulphate
column burden over Siberia is likely a result of enhanced oxidation rates of \( \text{SO}_2 \) due to the emissions of \( \text{NOx} \) from the shipping. However, some more analysis and sensitivity simulations are needed to confirm this.

![Figure 1. Calculated annual mean burden change of sulphate and BC aerosols for the Northern route (left) and the Sues route (right).](image)

Figure 2 shows the resulting change in global temperatures (again preliminary results) following a sustained ship transport along the two routes.

![Figure 2. Calculated annual and global mean temperature change (K) the Northern route (left) and the Suez route (right). The x-axis is years after start of emissions.](image)

The preliminary results indicate that the net impact of ship emissions following the two routes is actually the emissions along the shorter northern route lead to higher contribution to global warming even if the fuel use and thus the \( \text{CO}_2 \) emissions are lower. This is mainly due to the different sign of the contribution by the sulphate perturbation which is a combination of \( \text{SO}_2 \) emissions, changes in oxidation capacity and difference in clouds and surface albedo for the two regions.

**ACKNOWLEDGEMENTS**

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REFERENCES


NITRATE DYNAMICS IN THE ARCTIC WINTER SNOWPACK

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Keywords: NITRATE, SNOWSTUDIES, SVALBARD

INTRODUCTION

Snow can cover extensive parts of the northern hemisphere’s land masses and by this, set the condition for the terrestrial life in the north. The snow cover also acts as a large reservoir for atmospheric nutrients, such as the reactive nitrogen compounds: nitrate (NO₃⁻) and ammonium (NH₄⁺), on their transit into terrestrial systems. The NO₃⁻ found in snow and ice originates from atmospheric nitric acid (HNO₃), or particle bound nitrate (p-NO₃), which dissolves upon contact with snow. The HNO₃ in turn is believed to be the main sink of a range of atmospheric reactive nitrogen compounds (as nitric oxide, nitrogen dioxide and peroxyacyl nitrates) and where the deposition rate of HNO₃ is important for the overall atmospheric life time of these oxidized nitrogen’s. However, the snowpack NO₃⁻ reservoir has proved to not be an ultimate sink. Before its release to downstream ecosystems during snow melt, the snowpack NO₃⁻ is involved in an active atmospheric cycling. The understanding of NO₃ deposition, post-depositional, and melt processes are therefore of importance when investigating; the nutrient availability in the Arctic, interpreting ice core records, and assessing the chemistry of the Arctic atmospheric boundary layer.

CONCLUSIONS

For Ny-Ålesund snow the NO₃ deposition was found to be dominated by the incorporation and scavenging of HNO₃ and p-NO₃ during precipitation, and where this wet deposition shows large inter-annual variations due to sporadic events with high NO₃ delivery. Similar events of enhanced deposition were also evident for nitrate dry deposition due to elevated atmospheric HNO₃ and p-NO₃ concentrations and favourable boundary layer stabilities. Compared to wet deposition the dry deposition was found to be modest and only contributed to around 14% of the total NO₃ winter deposition. However, this dry deposition outnumbered any post-depositional loss of nitrate (as NO₃ photolysis or HNO₃ evaporation) during a surface snow spring campaign. Furthermore, the porous snow allows atmospheric processes to occur within its intra pore space, leading to a rapid re-deposition of oxidized nitrogen released from deeper buried snow layers or the soil below. Apart from wet and dry deposition, the only other process relevant for the overall NO₃ budget was found to be the final release of ions during snowmelt, which leads to a near complete removal of snow derived NO₃ from the small glaciers around Ny-Ålesund.
Figure 1. Nitrate processes important for Ny-Ålesund snow.

ACKNOWLEDGEMENTS

This study is a sum-up of a 4 years PhD work, were the fieldwork has been funded through SSF and were several of the long-term monitoring programs in Ny-Ålesund has been used. Furthermore, the project has benefitted from extensive collaboration with several of the institutes working in Ny-Ålesund (IIA-CNR, ISAC-CNR, NILU, AWI, NPI and ITM).
BOREAL ECOSYSTEMS AS MODIFIERS OF ATMOSPHERIC CHEMISTRY –
A SET OF PROCESS STUDIES AT SMEAR II STATION

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Keywords: BIOGENIC VOC EMISSIONS, BOREAL ECOSYSTEMS, SEASONALITY, ENCLOSURE MEASUREMENTS

INTRODUCTION

Compared to warmer regions, the boreal ecosystems are relatively inefficient as volatile organic compound (VOC) sources. However, due to their large aerial coverage, their contributions are both regionally and globally important. The strong seasonality, characteristic for boreal regions, is reflected in the physiological changes in important vegetation processes, such as growth, photosynthesis and transpiration, and has significant consequences for the role of these ecosystems as sources for precursors to atmospheric reactions.

METHODS

At the SMEAR stations, one of our main goals is to understand how vegetation processes control the carbon and water fluxes, including those of reactive precursor gases. Field measurements on VOC exchange between ecosystems and atmosphere at the SMEAR II site in Hytiälä Forest Research Station, southern Finland, have been conducted for over 10 years with both campaign-wise and continuous measurements. The online analysis of emissions with PTR-MS (proton transfer reaction mass spectrometer) and dynamic enclosures (Fig 1) has proven to be an efficient tool for detecting functional relationships between environmental factors (e.g. temperature, irradiation) and vegetation processes occurring at timescales of a few seconds, such as photosynthesis, transpiration and emissions of VOCs. The GC-MS (gas chromatograph-mass spectrometer) allows detailed speciation of compounds and thus offers means to reveal the concentrations of different terpenoids that influence the air reactivity.

Figure 1. Dynamic enclosures for VOC emission measurements. (a) two branch enclosures, (b) a stem enclosure, (c) a floating enclosure over a lake.
We have determined the accuracy of the dynamic chamber systems for measuring VOC emissions by creating a known source of different VOCs inside the chamber and measuring the concentration dynamics in the chamber (Kolari et al., 2012). The concentrations are underestimated by 5-30%, depending on enclosure type, measured compound and humidity inside the enclosure. However, by optimizing the measurement conditions we are able to obtain good repeatability and reduce the bias in the flux determination. More detailed descriptions of methods are presented in Aaltonen et al. (2012a), Tarvainen et al. (2005) and Vanhatalo et al. (ms in preparation).

RESULTS AND DISCUSSION

Terpenoids (isoprene, monoterpenes and sesquiterpenes), methanol and acetone are the main biogenic emissions, constituting also the vast majority of all emitted compounds in boreal regions (Guenther et al., 2012, Oderbolz et al., 2013). In short term, and especially during non-stressed mid-summer conditions, the emissions of monoterpenes from trees show clear temperature dependence, owing to the exponential relationship between compound volatility and temperature (e.g. Guenther et al., 1993, Tarvainen et al., 2005). Isoprene emissions are also closely connected to irradiance, as a result of the direct link between isoprene emission and synthesis from photosynthetic products. Under periodic stresses, e.g., drought, emissions from forest can change considerably (Fig. 2).

In addition to the short term drivers, VOC emissions are responsive to medium-term changes in environmental conditions, which may affect the emission capacity, storage pools, shape of the light response as well as the temperature optimum of emissions (Guenther et al., 2006, Arneth et al., 2008, Lappalainen et al., 2012). Our observations show that large seasonal variability in monoterpen-producing enzyme activities reflects the plant’s dynamic, inherent emission capacity and storage pool sizes (Fig. 3, Vanhatalo et al., manuscript in preparation).

Figure 2. Temperature vs. monoterpene emission rate (calculated with the Guenther type exponential relationship) from Scots pine branches in summer 2010. The emissions were affected by the extremely hot and dry latter part of July.

Figure 3. α-pinene emissions and synthase activities in needles of a Scots pine. Emissions are fairly stable over the year, although synthase activities vary a lot.
While the main source of VOCs is the foliage, significant quantities of VOCs are also originating from other sources in boreal ecosystems. The below-canopy compartment, i.e., tree trunks, ground vegetation, decaying litter, and soil processes, are important as sources of VOCs in particular during spring and fall, when fresh litter is creating a large source in the field layer (Aaltonen et al., 2011, 2012b). The tree stems can also form an important source of mono- and sesquiterpenes in the subcanopy air. Our first measurements indicate that in the transition time in early spring, high emission peaks may be connected to stem water transport capacity and potentially indicate freeze-thaw related changes in membrane permeability (Fig. 4, Vanhatalo et al., manuscript in preparation). Specifically, high sesquiterpene emissions were detected from the stem.

![Figure 4](image)

Figure 4. Stem and shoot monoterpene emission rates (a) and the diameter change in stem (b) in April 2012. Rapid change in phloem diameter coincides with a burst in emissions from the stem.

The forest floor plays a substantial role (from a few per cents to several tens of per cents, depending on the season) in the total VOC emissions of the boreal forest ecosystem. Highest emissions are measured in fall, due to the decaying litter (Aaltonen et al., 2011). Somewhat surprisingly, the wintertime fluxes within the snowpack can be equal to those from the soil during warmer periods, and soil seems to be an active source for VOCs even in winter. After winter storms when large amounts of litter are accumulating in the snow, concentrations may exceed the average concentrations manifold (Fig. 5, Aaltonen et al., 2012a).
Figure 5. Mono- and sesquiterpene concentrations inside snowpack at three heights from the ground surface (0 cm = closest to ground) in two winters (a, c: 2008-2009, b, d: 2010). In February 2010, abundant litterfall due to heavy snow damage caused extremely high concentrations to accumulate inside the snow.

Our recent studies show that the lake water can also be a substantial source for many VOCs. In several campaigns at the lake-SMEAR (lake Kuivajärvi), a humic lake nearby the SMEAR II forest, we discovered that the chemical composition of emissions and also the flux rates are rather similar to those measured from the forest floor (Sjöblom 2012, Aaltonen et al., 2011). We also discovered that the aquatic fluxes were largest during night-time, indicating either a specific nocturnal source for VOCs or an effect of transport phenomena between the lake and the boundary layer above (Fig. 6, Bäck et al., manuscript in preparation).

Figure 6. Emissions of mono- and sesquiterpenes, measured from the floating chamber at the lake Kuivajärvi in August 17-26, 2011
Estimates of emissions from vegetation are traditionally obtained for mature leaves under standard (constant) conditions to yield standard emission potential values (‘Guenther approach’), which then are used as model parameters. However, seasonality (aside from direct temperature effect) has been recognized to strongly influence isoprene and monoterpane emission rates as well as the emission capacity. A particular feature in boreal regions is that evergreen vegetation is dormant in winter, but recovers from dormancy when temperatures rise in spring. Our measurements (Fig 7, Aalto et al., submitted manuscript) show that the growth processes induce extremely high emissions of VOCs from buds and growing shoots, and that the temperature response for these is very different from that in previous year’s shoots. Buds and new shoots make up a small biomass in the beginning of the growing season, but their absolute contribution to the emissions from foliage is 50-75% for monoterpenes, 25-50% for methanol, 25% for acetone and 25-50% for isoprene/MBO. Interestingly, the maximum emission rates for monoterpenes are observed before growth even starts, which potentially could be linked to the high new particle formation events in early spring in the boreal forest.

![Figure 7. Temperature responses of monoterpane emissions from a mature shoot and from a new shoot with bud and growing needles, spring and summer 2010. The exponential relationship is fitted to the new shoot emissions in spring.](image)

**CONCLUSIONS**

With our comprehensive measurement setup and high temporal resolution, we are able to disentangle the ecosystem compartments and functions that contribute to production and emissions of atmospherically important reactive gases. This is valuable for clarifying the responses of VOC fluxes on changes in the environmental drivers, as they may affect different processes in a very different manner. The seasonal activity changes in vegetation in particular seem to play an important role in determining the leaf and stand scale VOC exchange, and thus a straightforward semi-empirical parameterization based on the maximum activity period in midsummer leads to erroneous emission estimates.

**ACKNOWLEDGEMENTS**

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REFERENCES


ATMOSPHERIC DUST MEASUREMENT IN ICELAND (ADMI 2013)

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Keywords: PARTICLE NUMBER CONCENTRATION, PM FRACTIONS, DUST STORM, DUSTTRAK.

INTRODUCTION

Iceland is an active source of natural dust in one of the main atmospheric transport pathways to the Arctic. Long-term frequency of atmospheric dust observations has been investigated in detail for NE Iceland (Dagsson-Waldhauserova et al., 2013a) and for the southern part of Iceland ((Dagsson-Waldhauserova et al., 2013b). An annual mean of 16.4 dust days was observed in NE Iceland and about 17.9 dust days occurred annually in southern part of Iceland in 1949-2011. Together, there were 34.3 dust days per year on average which places Iceland among the major dust areas in the world. The local dust sources have been identified as volcanic sandy deserts, ice-proximal areas and large glaciofluvial outwash plains, but sandy areas cover >22% of the country (Arnalds, 2010). Such barren surfaces are often influenced by strong winds resulting in frequent dust re-suspension. Icelandic dust storms are among the most severe wind erosion events recorded on Earth (Arnalds et al., 2013).

Locally impaired air quality due to dust re-suspension has been monitored for about a decade, but measurements cover only the total Particulate Matter (PM) mass concentrations. To understand better the physical properties and health impacts of dust events, in situ measurements of size segregated particle mass concentrations and number size distributions of dust aerosol are needed. The Charles University in Prague, the Agricultural University of Iceland and the University of Iceland will conduct in situ measurements of the physical characteristics of the Icelandic dust aerosol towards the Arctic in summer 2013 (the ADMI 2013 project-Atmospheric Dust Measurements in Iceland).

In this paper the methods and preliminary results on in situ measurements of mass concentrations in four size fractions of Icelandic dust aerosol are provided. An attempt is made to relate the results to human health and Arctic climate.

METHODS

Two instruments that record airborne dust concentration were provided by the Charles University in Prague and transported to Iceland. The TSI 8520 DustTrak Aerosol Monitors (DustTrak, Figure 1) are light-scattering laser photometers that measure aerosol mass concentrations in range 0.001 to 100 mg/m³ for particles ranging in size from 0.1 to 10µm. The particle concentrations recorded by DustTrak have been found as a reasonably accurate measure of dust storms in Arizona, USA, and in Australia (Jayrante et al., 2011). Both DustTraks are portable and enable us to measure a vertical profile of dust event.
CONCLUSIONS

We provide the preliminary results of in situ atmospheric dust measurements in Iceland in August 2013. The particle mass concentrations in four size fractions of dust event in the Arctic/Subarctic region have been investigated. The estimated mass concentrations for dust events of different severity are shown in Table 1 (Dagsson-Waldhauserova et al., 2013a). The health impacts of Icelandic dust aerosol are discussed based on the particle mass concentrations in segregated fractions. Physical properties and observations of dust events in Iceland have shown that not only regional air quality in Iceland (“Reykjavik haze”) is being impaired, but dust particles are transported over the Atlantic and the Arctic Ocean more than 1000 km at times.

<table>
<thead>
<tr>
<th>Dust event class</th>
<th>Visibility (km)</th>
<th>PM$_{10}$ concentration ($\mu$g/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Severe dust storm</td>
<td>\leq 0.5</td>
<td>31027</td>
</tr>
<tr>
<td>Moderate dust storm</td>
<td>0.5-1.0</td>
<td>8209</td>
</tr>
<tr>
<td>Severe haze</td>
<td>1.0-5.0</td>
<td>1265</td>
</tr>
<tr>
<td>Moderate haze</td>
<td>5.0-10.0</td>
<td>368</td>
</tr>
<tr>
<td>Suspended dust</td>
<td>10.0-30.0</td>
<td>126</td>
</tr>
<tr>
<td>Moderate suspended dust</td>
<td>30.0-70.0</td>
<td>52</td>
</tr>
</tbody>
</table>

Table 1. Estimated PM$_{10}$ concentrations of dust events of different severity based on visibility parameter in Iceland. Mean visibility of each dust class is recalculated into PM$_{10}$ concentration using the formula for steppe areas in China and the formula for the Saharan dust (Dagsson-Waldhauserova et al., 2013a).

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REFERENCES
STUDY ON THE CCN ACTIVATION AND STRUCTURE OF SOLUBLE, INSOLUBLE AND MIXED PARTICLES

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Keywords: silica, coating, CCN activation

INTRODUCTION

The atmosphere of the Earth contains numerous gases and aerosol particles which are defined as suspended liquid and solid particles with different sizes, shapes, and chemical compositions. Atmospheric aerosols have several important environmental effects (Jacob, 1999). Aerosol-cloud interactions cause the largest uncertainty in predictions of the future climate (Riipinen et al., 2012). To reduce this uncertainty we need to improve the understanding on how aerosol particles turn into cloud condensation nuclei (CCN) and furthermore to cloud droplets.

Insoluble atmospheric particles can act as efficient cloud condensation nuclei like soluble aerosols if they acquire some amount of deliquescent material. In the recent years, theoretical and experimental studies have been done on CCN activation of insoluble particles (Sorjamaa and Laaksonen, 2007; Kumar et al. 2009, 2011a and 2011b). Kumar et al. (2011a) reported laboratory measurements of CCN activity and droplet activation kinetics of insoluble mineral and dust particles. Kumar et al. (2011b) studied particle size distributions, CCN activity, and droplet activation kinetics of particles otherwise similar as in Kumar et al. (2011a) but generated using a wet method.

In this study, laboratory measurements were conducted on the particle size distribution, particle mass, morphology and CCN activation of pure soluble and insoluble particles as well as mixed ones. Aerosol particle mass analysis was used to determine the effective densities and shape factors of the particles. The CCN results were analysed and compared to the theoretical calculations using the framework introduced by Kumar et al. (2011b).

MEASUREMENTS

Pure and mixed soluble-insoluble particles were generated and analysed in this study. Fumed silica (SiO2, AEROSIL-90) was used as the insoluble particle. Three different kinds of species were used as soluble particle material: a salt (ammonium sulphate), a sugar (sucrose), and a protein (bovine serum albumin known as BSA). Particles were produced using the atomization-drying method (for details, see Keskinen et al., 2011). The solute content in the water suspension was 0.06 wt%. For mixed particles, the ratios of soluble component to silica were 1:19, 1:9 and 1:3, so the fractions of soluble species were 5%, 10% and 25% of total particulate mass in the atomized solution. Particle number distribution
measurements were made using a scanning mobility particle sizer (SMPS). The structure of the atomized and pure and mixed particles from aqueous suspension after drying was defined by transmission electron microscopy (TEM). Mass analysis of size selected agglomerated particles was conducted using a set-up consisting of a differential mobility analyser (DMA) followed by an aerosol particle mass analyser (APM). In this way, we obtained an estimate of the effective density of produced particles. The APM provides a direct relationship between applied voltage, rotation speed and the particle mass, and effectively operates as a mass spectrometer (Liu et al., 2012).

Size-resolved CCN activity was carried out using the Scanning Mobility CCN Analysis (SMCA), where the DMA used for aerosol classification is operated in scanning voltage mode with dry particle diameters from 30 to 200 nm in supersaturation (SS) range from 0.1 to 1.5. The DMT CCN counter was used to measure the activated fraction of the aerosol at given supersaturation.

**THEORY**

κ-Köhler theory (Petters & Kreidenweis, 2007) was used to estimate the critical supersaturations of pure ammonium sulphate, sucrose and BSA species. Critical supersaturations of pure silica particles, on the other hand, were calculated using the FHH adsorption activation theory (Sorjamaa and Laaksonen, 2007 and Kumar et al., 2009 & 2011a). For mixed soluble and insoluble particles Kumar et al. (2011b) introduced a shell-and-core model with the core representing insoluble dust and shell consisting of a layer of soluble salt. In this case the relationship between water saturation ratio \( S \) and particle size and composition can be expressed as:

\[
s = \frac{4\sigma_w M_w}{RT \rho_w D_p^3} \left( \frac{\varepsilon_p D_h^3}{(D_p - \varepsilon_p D_h^3)} \right) - A_{FHH} \left( \frac{D_p - \varepsilon_1 D_h^3}{2D_h^3} \right)^{-B_{FHH}},
\]

where \( s \) is the saturation ratio, \( \sigma_w \) is the water surface tension, \( \rho_w \) is the water density, \( M_w \) is the molar mass of water, \( R \) is the universal gas constant, \( T \) is the temperature, \( D_{dry} \) is the dry particle diameter, \( D_p \) is the droplet diameter, \( D_{H2O} \) is the diameter of water molecule, \( \kappa \) is the hygroscopicity parameter of soluble particles, \( \varepsilon_i \) and \( \varepsilon_i^{core} \) are the insoluble and soluble volume fractions in the dry particle and, \( A_{FHH} \) and \( B_{FHH} \) are the FHH adsorption isotherm parameters.

The mass corresponding to each rotation speed and measured voltage by APM is calculated by the following equation (Park et al., 2003):

\[
m = \frac{qV}{r^2(\omega)^2 \ln(r_2/r_1)},
\]

in which \( m \) is the particle mass, \( \omega \) is the APM angular speed, \( V \) is the applied voltage, \( q \) is the particle charge, \( r_1, r_2 \) and \( r \) are inner, outer and rotating radii at the equilibrium, respectively.

Once the mass of the particles has been estimated, their density can be calculated from

\[
\rho = \frac{m}{\pi d_{me}^3/6},
\]

where \( d_{me} \) is the mobility diameter of the particles.

After plotting the number concentration of the particles vs. particles density (corresponding to different voltages of the instrument) for each size of particles, the peak value of each curve shows the effective density (\( \rho_{eff} \)) of the size selected particles.

**PRELIMINARY RESULTS**

Aerosol particle size distributions

The SMPS measurements yielded the number size distributions for silica particles coated with \((NH_4)_2SO_4\) sucrose and BSA. Figure 1 shows the size distribution of particles made of pure fumed silica,
pure sucrose, and mixtures of silica and different coating amounts of sucrose. Particles made of pure sucrose have a mean diameter of about 50 nm, and the particles made of pure silica around 150 nm. For the silica particles coated with different amounts of sucrose the size distribution show two peaks, one below 30 nm and the other one at around 150 nm.

Figure 1: SMPS data on the number size distributions of silica particles coated with sucrose.

Particles composing the first peak of the bimodal distribution curves are likely pure soluble particles, since their mean diameter is smaller than that of the pure silica particles. We therefore conclude that the second peak of the bimodal distribution curves represent the silica particles coated with the soluble species.

Particle morphology

Fig. 2 shows the morphology of the atomized particles. The pure sucrose particles were spherical (Fig. 2a). Previous measurements for ammonium sulphate particles have also suggested shapes not far from spherical. In contrast, the pure BSA particles formed agglomerates, and branch-like structures between agglomerated spheres (Fig. 2b). Pure silica particles were clearly agglomerates with larger (around 50 nm) and smaller (~15 nm) primary particles (Fig. 2c) as expected for flame produced silica (Keskinen et al., 2011). As silica and BSA get smaller, the particles get more compact and more spherical. The morphology differences for mixed and pure silica were not visible by TEM imaging. The mixed particles appear similar to pure silica agglomerates (Fig. 2d, e and f).

Results from particle mass analysis

The TEM images showed that silica and BSA particles are agglomerates, but from the two dimensional images with a few particles only it is difficult to draw any quantitative conclusions regarding their shape factors and effective densities. To get a better understanding of these features, we performed particle mass analysis. Fig. 3 presents the number concentration of 100nm silica and BSA particles for different particle densities (calculated from corresponding APM voltage). Gaussian distributions were fitted to get the peak values for the densities of DMA size selected particles, representing the effective densities of 100 nm particles in these plots. The peak value is equal to 815 kg/m$^3$ for silica particles, and 370 kg/m$^3$ for BSA particles.
Fig. 2: TEM images for (a) pure sucrose particles, (b) pure BSA particles, (c) pure silica particles, (d) mixed silica-BSA particles, (e) mixed silica-sucrose particles, (f) mixed silica-ammonium sulphate particles (red circles shows particles with the diameter of 100 nm and green ones represents 200 nm particles)

Fig. 3: The number concentration distribution of particles classified by APM in terms of particles density (proportional to voltages applied in the APM) for 100 nm particles classified by DMA. (a) Pure silica particles, (b) pure BSA particles

CCN activation results

Kumar et al. (2011a) (quartz silica) and Keskinen et al. (2011) (fumed silica, AEROSIL-300) suggested quite different values for FHH adsorption parameters of silica. To compare our results (Fumed silica, AEROSIL-90) of the pure silica activation to those studies, we fitted the FHH adsorption parameters of
silica. $A_{FHH}$ and $B_{FHH}$ values of 0.83 and 1.23 explained our results on the activation diameter vs. critical supersaturation. The results do indicate, however, that our results are a bit better in line with the work of Kumar et al. (2011a) than Keskinen et al. (2011).

For estimating the critical supersaturation of pure soluble particles, $\kappa$-Köhler theory was used. A number of studies have been published on the CCN properties of pure ammonium sulfate. We therefore only investigated the CCN properties of pure sucrose and BSA particles. In general, $\kappa$-Köhler theory gave good results with the CCN activation of pure BSA and sucrose particles. The activation ratio curves (the ratio of activated particles to total particles) were calculated for particles with the dry diameters of 100, 120, 150, 200 and 250 nm and different ratios of soluble to insoluble materials. After estimating the critical supersaturations (corresponding to 50% activation) from the activation ratio curves for each mixture and each dry diameter, the critical supersaturation curves were drawn for different dry diameters. Fig. 4 shows the experimental and calculated supersaturation of pure and mixed silica and BSA particles. It can be seen that the experimental critical supersaturations deviate more from the theoretical values at small particle sizes, and at high BSA mass ratios. Similar deviations between the experimental and calculated critical supersaturation in smaller diameters were also seen in the particles mixed with sucrose and (NH₄)₂SO₄. The deviations can possibly be explained with the low effective densities, but for definite conclusions we need to determine the effective densities for all particle sizes, which is work still ongoing.

![Fig. 4: Experimental and calculated and critical supersaturations for silica + BSA particles for different particle dry diameters using adsorption activation theory (shell-and-core model).](image)

**DISCUSSION**

We measured the particle size distribution, particle mass, morphology and CCN activation of insoluble fumed silica particles coated with (NH₄)₂SO₄, sucrose and BSA with an SMPS. The results showed that the pure particles formed unimodal distribution curves, while the mixed particle distributions were bimodal. The SMPS measurements showed that the particles in the smaller modes of the bimodal distributions consisted of pure soluble materials, and the diameters of these particles were less than 100 nm.

The CCN activity measurements were conducted at various supersaturations up to 1.5%, and activation ratio curves were prepared for the studied particles. The experimental data were compared to theoretical predictions using the FHH adsorption theory (e.g. Sorjamaa and Laaksonen, 2007) for the pure silica particles, the $\kappa$-Köhler theory (Petters and Kreidenweis, 2007) for the pure soluble particles, and the combination of these two (Kumar et al., 2011b) for the mixed particles. The pure soluble particles, specifically sucrose and BSA, followed the predictions of $\kappa$-Köhler theory. In the case of BSA particles a small deviation was observed for the particles less than 150 nm. The pure
silica, however, showed a deviation from the FHH theory. The reason for this deviation is not clear and needs further investigation.

For the mixed particles, the experiments showed that by increasing the soluble fraction, the particles activated at lower supersaturations. But for these particles at smaller sizes, the observed critical supersaturations were less than the estimated ones from the shell-core model by Kumar et al. (2011). The critical supersaturation of pure BSA particles in diameters less than 150 nm are higher than the particles with 25% BSA. The adsorption of BSA molecules on silica particles may have influenced their structural stability, which is a possible reason for the different activation behavior of coated particles compared to the pure BSA. Curiously, ammonium sulfate and sucrose showed similar behavior at the small (< 150 nm) particle diameters. The reason for this behavior needs further investigation.

In the current step of this study we are trying account for the effective density and shape factor of the agglomerated particles, in order to reduce the deviation between the experimental activation curves especially for particles smaller than 150 nm.

ACKNOWLEDGEMENTS

All experiments have been conducted in the department of Applied Physics at Kuopio campus of the University of Eastern Finland. Financial support from CRAICC and Vetenskapsrådet is gratefully acknowledged.

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LOCAL SCALE UNDER ICE CO₂ AND CH₄ PROCESSES IN BOREAL LAKES
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Keywords: Cryosphere, Climate Change, Greenhouse gases (Carbon Dioxide, Methane), Lakes.

INTRODUCTION

The impacts of climate change are particularly pronounced at northern latitudes, directly affecting ice cover duration and surface water temperatures of arctic and boreal lakes (Benoy et al., 2007). Alterations to ice dynamics will have profound effects on the mechanisms that control carbon dioxide (CO₂) and methane (CH₄) accumulation in lakes during ice cover. Lake ice acts as a barrier to greenhouse gases (GHG) efflux to the atmosphere, modifies oxygen tension in the water column and sediment and decreases light penetration to surface waters (AMAP, 2011). Since arctic and boreal regions are poised to experience significant changes to ice duration and dynamics and increase in winter precipitation (Prowse et al., 2011), it is of utmost importance, in terms of understanding the land-atmosphere carbon balance, that we advance the understanding of climate-induced cryosphere changes to freshwater lakes and subsequent effects on lake GHG emissions. The ultimate goal is to understand these changes on a regional scale (i.e., arctic and boreal), although, detailed high frequency local scale studies are needed to understand seasonal variability in under ice carbon processes which will give insight into processes that occur on a regional scale.

Our current knowledge of CO₂ and CH₄ accumulation in lakes (i.e., sediment, water and ice) during ice cover and consequent GHG emissions at ice melt is limited in temporal and spatial resolution. It has been suggested that strong vertical stratification during winter leads to highest CH₄ and CO₂ concentrations at bottom waters near sediments (Bastviken et al., 2008; Rantakari & Kortelainen, 2005), however, high concentrations of CH₄ have been found to be trapped in ice (Walter et al., 2006) which could also lead to high concentrations of CH₄ and CO₂ (if oxidized) in surface waters at ice melt. During the open water season, CO₂ rates are mainly controlled by differences between in lake respiration and photosynthesis, phototransformation and sedimentation, while CH₄ is a function of production in the sediment, oxidation in the water column, and flux patterns. However, during ice cover in lake processes change directly influencing CO₂ and CH₄ accumulation rates; as lake experience inverse stratification (sediment temperatures around 4°C and surface waters near 0°C), decreased surface water light exposure, minimized wind effect and water currents, and increased oxygen depletion towards bottom waters (e.g., Striegl et al., 2001). Thus, it is important to monitor under ice in situ lake parameters in relation to CO₂ and CH₄ concentrations in order to detect how ice dynamics indirectly and directly influences CO₂ and CH₄ accumulation and GHG emissions at ice melt.

METHODS

Two local scale subprojects were carried out during the winter field season of 2013 to assess temporal and spatial CO₂ and CH₄ accumulation in a boreal lake under ice cover.

Project 1 (Lake Gäddtjärn): Under ice daily CO₂ accumulation

At Lake Gäddtjärn, a humic small boreal lake (213 ha) situated in mid Sweden (59.8592 °N, 15.1834 °E) at an altitude of 263 meters above sea level, temporal high frequency CO₂ accumulation and spatial carbon quantity were measured during the ice cover period and subsequent ice break up. Under ice surface water (~2m) pCO₂ at the deepest point on Lake Gäddtjärn (~10m) was monitored in-situ continuously over a period of approximately three and a half months, 20 January – 7 May (Error! Reference source not found.). Two different sensors, GMT220 Series Carbon Dioxide Transmitters
(Vaisala) and SAMI²-CO₂ (Sunburst sensors), measured hourly CO₂ concentration in the water. The Vaisala sensor was protected with a polytetrafluoroethylene (ePTFE) tube (International Polymer Engineering) that is impermeable to water but permeable to CO₂ and connected to a datalogger (Campbell Scientific CR1000) to track CO₂ (e.g., Johnson et al., 2010). In addition a probe measuring pH, dissolved oxygen and temperature at ~4m (YSI), a light sensor suspended below ice cover (HOBOWare), and a temperature chain measuring every 1 m to a total depth of 10 m (TOJO Skogsteknik Soil temperature probe TO3R) were deployed.

In addition, lake water was sampled 6 times during ice cover (December—April) and once during spring melt (May) to assess the spatial variability in carbon quantity across the lake. Surface waters were collected at six different locations on the lake; inlet 1, inlet 2, outlet, middle, shore and deepest point. In addition, at the deepest point, samples were collected at varying depths; surface, 2m, 4m, 6m and 8m. Upon collection, water samples were stored in the dark until analysis back at the lab. Partial pressure of carbon dioxide (pCO₂) was analysed directly using the headspace equilibration method (e.g., Sobek et al., 2003). A known ratio of water to ambient air was equilibrated in the syringe by shaking it vigorously for one minute. The equilibrated air was then analysed on a portable infrared gas analyser (IRGA, EGM-3 PP Systems). pCO₂ was calculated according to Weiss (1974) using the appropriate Henry’s constant after correcting for temperature and atmospheric pressure as well as the amount of CO₂ added by the ambient air. Further, dissolved organic carbon (DOC) concentrations (filtered through GF/F glass fibre filters (0.7 μm, Whatman)) and dissolved inorganic carbon (DIC) concentrations were determined using a total organic carbon (TOC) Analyser (Sievers 900) equipped with a membrane-based conductivity detector.

**Project 2 (Lake Erken): CH₄ accumulation at the water-ice interphase**

At Lake Erken, a relatively large (2400 ha), mesotrophic (TP 27μg/L), thoroughly limnologically investigated lake, temporal CH₄ and CO₂ accumulation patterns in lake water and ice were spatially tracked throughout the ice cover period. At three different occasions during ice cover, samples were collected from the shore, transition and pelagic zone of Lake Erken, where ice and water from the surface, middle and bottom was collected. In addition at the deepest point of the lake (21 m) ice and waters were collected from 0cm, 20cm, 40cm and 60cm, specifically targeting areas with CH₄ formation under ice (i.e., methane bubbles). A floating vertical stick with stopcocks attached to tubing was submersed under the ice at a distance of 2 m from the targeted bubble and water was extracted via a syringe.

Following the methods outlined in Bastviken et al., (2008) and Sobek et al., (2003), respectively for CH₄ and CO₂, equilibrated headspace (i.e. equilibrated air from known water to ambient air ratio vigorously shaken for one minute) was injected into pre-capped bottles filled with bubble free salt solution for CH₄ and syringes for CO₂. Samples were stored in the cool dark until analyzed (CO₂ was immediately sampled upon returning from the field and CH₄ was sampled within a week) on the gas chromatograph (GC). Ice cores from the water surface up 20 cm were collected with an ice auger (~55 mm diameter) and transported frozen to laboratory in sealed bags. In a nitrogen glove box (O₂ < 1.5%) the ice cores were placed in tubes, flushed with nitrogen, capped and allowed to melt. Once the ice was melted the ratio of water to air in the tubes was recorded and the headspace and melt water was equilibrated (e.g., Phelps et al.,1998) . The equilibrated air was then measured on the GC.

**CONCLUSIONS**

**Project 1 (Lake Gäddtjärn):**

From preliminary results it appears under ice surface water CO₂ concentrations do not consistently accumulate over the ice cover period. Although, pCO₂ in surface waters is significantly higher at the end of ice cover compared to the beginning of ice cover, surface water pCO₂ peaks in February. Contrary, pCO₂ in bottom waters appears to accumulate consistently over the ice cover period. This contrast, between under ice surface water and bottom water CO₂ accumulation, suggests ice and snow cover dynamics on the lake and snow in the surrounding
catchment may influence surface water $p$CO$_2$. In addition, surface water $p$CO$_2$ varied across the lake with highest average $p$CO$_2$ at the outlet of the lake, which coincided with highest $p$CO$_2$ at the outlet stream during winter. Thus it is likely CO$_2$ in surface waters exits the lake via the outlet during ice cover (although this may not be the case in lakes with longer resident’s time). However, a consistent pattern in CO$_2$ accumulation and reduction was not observed over the whole ice cover period, suggesting snow and ice dynamics (e.g., cracks in ice, light penetration, snow melt) may also influence surface water CO$_2$ concentrations.

Project 2 (Lake Erken):

From our preliminary results, across a spatial transect (from littoral to pelagic zone) we found that CO$_2$ increased with depth while CH$_4$ did not show consistent differences between surface, middle and bottom waters. Average CO$_2$ and CH$_4$ concentrations were highest in the pelagic zone, which was the only zone that experienced a strong stratification with anoxic bottom waters. At the ice-water interface (i.e., targeting for CH$_4$ bubbles) only one of three occasions showed a significant difference between CH$_4$ concentrations at fine scale gradient from just below the ice to 60cm (Figure 2). At this one occasion CH$_4$ decreased by more than 50% from 0 cm to 20 cm, suggesting CH$_4$ can accumulates at discrete gradients within and below the ice boundary layer but this accumulation is not consistent throughout the ice cover. Further, although concentrations were low (CH$_4$$<$$ 0.5$μM) we observed CH$_4$ consistently trapped in ice cores throughout the sampling period. Our preliminary results suggest it is important to consider CH$_4$ accumulation at the ice-water interphase (less so for CO$_2$), although CH$_4$ concentrations were low in this lake, the observed CH$_4$ accumulation at discrete gradients within and below the ice could be greatly affected by changes to ice cover dynamics.

To conclude, from these two local scale studies on boreal lakes during ice cover our results suggest CO$_2$ concentrations are highest, and accumulated in bottom waters. However, surface water CO$_2$ concentrations increase from the early ice period but do not accumulate over time. Our study was unable to distinguish where surface water CO$_2$ ends up but we suggests CO$_2$ can flow out of the system via outlet streams or ice cracks, be transformed via photo-process below ice or influenced by hydrological pathways (i.e., stream and snow melt) entering the lake. Further research needs to be carried out to make more robust conclusions about surface water CO$_2$ concentrations under ice cover. Further, our study suggest CH$_4$ is present at the water-ice interphase and further investigation is warranted to understand the fate of CH$_4$ at this discrete gradient (i.e., oxidation to CO$_2$ or evaded as CH$_4$). Generally, our results suggest ice cover dynamics play a role in CO$_2$ and CH$_4$ accumulation in lakes and therefore further changes to ice duration and dynamics on arctic and boreal lakes will affect annual GHG emissions from these lakes.
Figure 1. Under ice surface water (~2m) $pCO_2$ and water temperature at the deepest point on Lake Gäddtjärn (~10m) was monitored *in-situ* continuously over a period of approximately three and a half months, 20 January – 7 May.

Figure 2: CH$_4$ concentrations at a discrete water-ice gradient (0-60cm below ice) at three different sampling occasions during ice cover on lake Erken.
ACKNOWLEDGEMENTS

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Phelps, A. R., Peterson, K. M., & Jeffries, O. (1998). Methane efflux from high-latitude lakes during spring ice melt the taiga lakes, indicated a large pulse of methane released during the period of ice melt and period in 1996 predicted an efflux g CH during the same compared with g CH for the remainder of the summer This, 103.


How robust are Holocene treeline simulations? A model–data comparison in the European Arctic treeline region

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ABSTRACT
Treeline encroachments and retractions can provide global-scale feedbacks to the climate system, and treeline dynamics are therefore of great relevance for understanding global climate variability. To assess the accuracy of long-term treeline simulations based on the generalized dynamic vegetation model LPJ-GUESS, we simulate European Arctic treeline dynamics over the past 9000 years and compare the results with fossil-based reconstructions. The results show that while LPJ-GUESS is limited in its ability to capture species-level current treeline patterns and past dynamics, it is generally able to realistically simulate the Holocene coniferous treeline changes with a cutoff biomass carbon of 2 C kg / m². The model captures the northward expansion of the boreal forest during the mid Holocene and correctly simulates a treeline retreat in response to climate cooling during the last 3000 years. However, there are data–simulation disagreements particularly during the early Holocene, which mainly result from the differences between the two palaeoclimate model scenarios used to drive the simulations. We suggest that the spatial accuracy of the model could be improved by incorporating the influence of topographic features, the extent of the Arctic peatlands, the tree species life history characteristics, microclimate, and other ecological factors.

Keywords: Arctic treeline, LPJ-GUESS, fossil records, Holocene.

INTRODUCTION
Northward expansion of the treeline can in turn modify land–atmosphere interactions and provide feedbacks to the climate system. Replacement of tundra by forest decreases surface albedo and sequesters greater amounts of carbon from the atmosphere by increasing the carbon storage in soils and woody biomass. These mechanisms can provide both positive and negative feedbacks to
long-term temperature trends. The Lund-Potsdam-Jena-GUESS (LPJ-GUESS) model is a process-based dynamic vegetation model that has been widely used to simulate the structure and dynamics of terrestrial ecosystems from landscape to global scales. Here we test the ability of LPJ-GUESS to simulate the Holocene treeline dynamics in the European Arctic treeline region. This model is particularly advantageous for our study region because the treeline in northern Europe exhibits clear ecotone boundaries between the boreal forest and the tundra.

METHODS
Two LPJ-GUESS experiments were designed using climate data from ORBGHG (hereafter ORBGHG-s) and OGMELTICE (hereafter OGMELTICE-s) palaeoclimate simulations performed with ECBilt-CLIO-VECODE (see Renssen et al. (2009) for details). In the ORBGHG-s, LPJ-GUESS is driven by palaeoclimatic data with orbital and greenhouse gas forcings only. In OGMELTICE-s, the palaeoclimate simulation also includes orbital and greenhouse gas forcings, but additionally includes forcings resulting from the freshwater fluxes, albedo and topography of the Laurentide ice sheet.

CONCLUSIONS
Given the current strong warming of the Arctic climate, there is an acute need to understand how accurately and reliably the large-scale treeline shifts can be modeled. We tested the performance of the dynamic vegetation model LPJ-GUESS in Arctic Europe, where various types of fossil records have shown prominent treeline shifts during the Holocene. Our results show that the model is able to mimic these dynamics fairly accurately. However, the model simulations are sensitive to palaeoclimatic input data. The most conspicuous inconsistency is observed between OGMELTICE-s and the fossil records during the 9000 cal a BP, which are caused by the simulated too cold climate in the early Holocene. At 6000 cal a BP, when the Arctic treeline generally reached its northernmost position in Europe, the two simulations are more consistent with each other and agree well with the fossil data. It is also notable that although the model performs well in simulating the past dynamics of the Arctic treeline, it is less good in species-specific simulations of Pinus and Picea. In the simulation of the current treeline, Picea extends too far north and Pinus is underrepresented in northern Fennoscandia, although in reality the treeline in northern Fennoscandia is dominated by Pinus. The unrealistically southern limit of Pinus is to a great extent caused by competitive suppression by Picea, a shade-tolerant species, in the simulation, suggesting that the parameters that control the competition between the two species may need adjustments.
EFFECT OF BLACK CARBON ON THE SNOW ALBEDO IN NORTH EAST CHINA

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Keywords: Snow albedo, Black Carbon, Radiative Forcing

Black Carbon (BC) atmospheric particles originate from incomplete combustion of fossil fuel and biomass. When deposited on the surface, even small amounts of BC can reduce the snow albedo. However, the lack of observations and poor process understanding makes estimates of its climate impact uncertain.

We have conducted measurements of semi-continuous BC concentrations in snow surface and snow spectral albedo at CAS Research Station of Changbai Mountain Forest Ecosystem in North East China during three snow seasons 2009/10, 2010/11 and 2011/12. Preliminary results showed us that most of the BC is deposited through dry processes. The level of BC in the snow surface is very high so that a strong decrease of the snow albedo is expected but it is not seen in our measurements. The reason is that due to the cold and dry winter in that area, deposition of surface hoar crystals by condensation of vapour water onto the snow surface during the night is frequent. The formation of surface hoar does not include any BC particles so that the top layer of the snowpack is made of pure small ice crystals. This explains why our measurements show higher values than what should be expected using modeling study.

We will present our 3 years of data and compare our albedo measurements with modeling study in order to emphasis the role of the surface hoar deposition in Changbai station. Taking into account the meteorological conditions, it is therefore possible to better understand the effect of BC on the snow albedo according to its concentration and the physical properties of the snow surface.
A review of sea spray aerosol source functions using a large global set of data

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Keywords: Sea Spray, Aerosols, Source functions.

\section*{INTRODUCTION}

Sea spray aerosols (SSA) are an important part of the climate system through their effects on the global radiative budget both directly as scatterers and absorbers of solar and terrestrial radiation, and indirectly as cloud condensation nuclei (CCN) influencing cloud formation, lifetime and precipitation. In terms of their global mass, SSA have the largest uncertainty of all aerosols (Textor et al. 2006).

\section*{METHOD}

In this study we have reviewed 21 SSA source functions from the literature, several of which are used in current climate models, and we propose a new function. The FLEXPART Lagrangian model (Stohl et al. 2005) was run in backward mode from a large global set of observed SSA concentrations, comprised of several station networks and ship cruise measurement campaigns (see Fig. 1). FLEXPART backward calculations produce gridded emission sensitivity fields, which can subsequently be multiplied with gridded SSA production fluxes to obtain modeled SSA concentrations. The color scale in Fig. 1 show how the source regions for the stations cover the globe. This allowed to efficiently evaluate all 21 source functions at the same time. Another advantage of this method is that source-region information on wind speed and sea surface temperatures (SSTs) could be stored and used for evaluating their influence on SSA production.

\section*{RESULTS}

The main objective of this paper was to review the numerous existing SSA source functions, and evaluate them against observations within one model. Also, by correlation of SSA concentrations with source-region averaged 10-meter wind $U_{10}$ and temperature, the influence of these parameters on the produced SSA could be quantified. The main driver of SSA production is wind, and the best fit to the observation data could be obtained when the SSA production is proportional to $U_{10}^{3.5}$. A strong influence of SST on the production could be detected as well, although the underlying physical mechanisms of the SST influence remains unclear. For SST we obtain the best fit to the measurement data when SSA concentration is proportional to $0.031T+0.39$, where $T$ is the source average SST. A summary of how the different source functions performed against the observational
data is given in Table 1.

Based on the model source region average temperature and wind, an empirical fit was made to the data and a new source function obtained. The fit was made by using the model concentrations, observational data, ECMWF winds and the existing source function volume fluxes. Several variations of existing functions were tested, both by changing the mass of all aerosol sizes and by changing the wind speed dependence. The best fit to the data was obtained by using a modified SH98 (see Table 1 for reference abbreviations) source function, G13T. The original SH98 parameterization did not cover particles smaller than $D_p = 1 \mu m$. The modification was to add a lognormal particle distribution for accumulation mode particles. The added lognormal mode of particles was given the amplitude to best fit the collected source functions that cover accumulation mode, and was centered at 0.1 $\mu m$. It was tested with all available temperature dependencies (no temperature dependence, $0.031T+0.39$, the temperature dependence of J11T and S11T). The temperature weight of J11T fits the data the best and is therefore recommended as $T_W$. The new source function, with three lognormal modes is:

$$
\frac{dF(D_p, U_{10}, T)}{dD_p} = T_W \cdot [235 \cdot U_{10}^{3.5} \exp(-0.55[ln(T_{80}/0.1)]^2) \\
+0.2 \cdot U_{10}^{3.5} \exp(-1.5[ln(T_{80}/3)]^2) + 6.8 \cdot U_{10}^{3.5} \exp(-1[ln(T_{80}/30)]^2)]
$$

(1)

The source function Eq.(1), G13T, was modeled by the same method as the source functions in Table 1. Our new source function gives a global SSA production for particles smaller than 10 $\mu m$ of 9 $Pg \ yr^{-1}$ and is the best fit to the observed concentrations. Have the largest uncertainty of all aerosols, and limiting this uncertainty is an important task in climate models.
Table 1: List of all the source functions used in this paper. For sake of brevity, the acronym is used throughout the text. $D_p$ gives the validity size range in $\mu m$ dry diameter. Type is the method that the authors have used to produce the source function. Mean is the annual average global production averaged over the 25-yr of ECMWF data available, and $\pm$ is the difference in mass between maximum and minimum year, also in Pg. Bias is the modeled concentration compared to the PM$_{10}$ measurements in percent. Pearson’s r coefficient for $r_a$, the entire data set, $r_{pm10}$ the PM$_{10}$ observations only, $r_c$ the daily average measurements and $r_W$, all the week long observations. For the data subsets the mean station correlation is reported and not as for $r_a$ the correlation for the set of data as a whole.

<table>
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<th>Reference</th>
<th>Acronym</th>
<th>$D_p$</th>
<th>Type</th>
<th>Pg yr$^{-1}$</th>
<th>$\pm$</th>
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<th>$r_a$</th>
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<th>$r_c$</th>
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CONCLUSIONS

The novelty in this study lies in the source receptor relationships applied for SSA. While earlier studies have used local wind speeds and temperatures to connect SSA production and concentration, this study uses wind speeds and temperatures in the area where the aerosols are actually produced. Source functions are easily applied and can be compared to each other within the same backward modeling framework. By applying this method to all the SSA source functions we have found the following:

- Estimates of the SSA aerosol burden have a larger uncertainty than burden estimates for other aerosols combined (Textor et al. 2006). The large spread of more than 70 Pg yr$^{-1}$ between the ”best” SSA source functions found in this work reflects this. The reasons for this large spread within the source functions are not apparent, but may be related to the type of measurements the various source functions are derived from. The global annual budget of SSA is thus strongly dependent on what source function is applied.

- Based on a comparison of modeled and measured SSA concentration, our best estimate of the global production rate of SSA is 9 Pg yr$^{-1}$. The new source function G13T has an annual SSA production rate very close to this value.
• The best performing SSA production function with the best correlation is G13T (up to $r = 0.86$ for EMEP stations) and it also has the smallest bias between measured and modeled SSA concentrations.

• Correlation between measured and modeled SSA concentrations are much lower ($r = 0.22–0.54$) at stations that apply wind-sectored sampling than at stations with unconditional sampling ($r = 0.36–0.86$). This demonstrates that data obtained with sectored sampling are very difficult to use for quantitative analyses as the measurements do not represent a time-mean concentration.

• Wind speeds in the range $5–14 \text{ m s}^{-1}$ are very frequent and are responsible for about 80% of the global SSA production. Parameterizations of SSA production must therefore accurately capture the wind speed dependence especially in this wind speed range. A power law dependence where SSA production is proportional to $U^{3.5}_{10}$ was found to best describe the observed SSA concentrations.

• We found a clear dependence of SSA production on sea surface temperatures. SSA concentrations increases with temperature according to the relationship $0.031T + 0.39$. This temperature dependence is particularly important to explain the relatively high SSA concentrations found in the tropics. The temperature dependence of production of Jaegle et al. (2011) was found to be best able to account for the effect of temperature.

• Several of the reviewed source functions were incompatible with observations. Both in terms of correlation and mass concentrations. Thus the choice of SSA source function in any model must be carefully considered.

ACKNOWLEDGEMENTS

This work was supported by NordForsk as part of the Nordic Centre of Excellence Cryosphere Atmosphere Interactions in an Arctic Changing Climate (CRAICC). The authors also thank kindly Joseph M. Prospero for sharing his collected data. We also acknowledge and thank Tim Bates and Jim Johnson for sharing NOAA, PMEL data. Also the assistance of P. Eckhardt and A.G. Hjellebrekke with the EBAS database, and EMEP station data suppliers Margaret Ryan (Met. Eiyreann) and W. Aas (NILU) is acknowledged.

REFERENCES


IDENTIFICATION OF ORGANOSULFATES AND CARBOXYLIC ACIDS IN ARCTIC AEROSOLS

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Keywords: ORGANOSULFATES, ARCTIC, AEROSOL TRANSPORT

INTRODUCTION

The Arctic climate is sensitive to changes in radiative balance as evident by the on-going melting of sea-ice (IPCC, 2007; ACIA, 2005). Atmospheric aerosols are one of the key constituents in the climate system, influencing the radiative balance of Earth directly by reflecting or absorbing solar radiation and indirectly by acting as cloud condensation nuclei (CCN) (Kulmala et al., 2004). In contrast to greenhouse gases, their large variability in size and composition and short life time result in large uncertainty in understanding their role in climate system. The reflection, absorption and CCN properties of the aerosols are highly dependent on particle size and the chemical composition of the particles (Lohmann and Feichter, 2005; Andreae et al., 2004). In order to understand the present and future changes in the Arctic climate, the composition of atmospheric aerosols must be investigated. In this study we focus on the seasonal variation in the occurrence of organic aerosols. More specifically we present measurements of total organic matter (OM) and speciation of organic oxidation products from two Arctic sites (Station Nord and Zeppelin Mountain) during a full annual cycle. In the chemical analysis we focused on the speciation of three types of secondary organic aerosol (SOA) tracers: carboxylic acids, organosulfates and nitrooxy organosulfates from both anthropogenic and biogenic (monoterpines and isoprene) precursors. Our aim is to investigate their concentration levels and occurrence in Arctic aerosols throughout the year and study links between aerosol sources, sinks and atmospheric transport to and within the Arctic.

METHODS

Aerosol samples were collected during a full annual cycle at two Arctic sites. In 2008 weekly Total Suspended Particles (TSP) samples were collected using a low volume sampler at Zeppelin Mountain, Svalbard (78°54’ N, 11°52’ E, 478 m a.s.l) and in 2010 weekly PM10 samples were collected on quartz fibre filters using a high volume sampler at Station Nord, Greenland (81°36’ N 16°40’ W, 30 m a.s.l.). Samples were extracted in acetonitrile/water (90/10 V/V%) followed by analysis using a high performance liquid chromatograph coupled to a time-of-flight mass spectrometer (HPLC-q-TOF-MS) through an electro spray inlet. Carboxylic acids were identified and quantified using authentic standards (Sigma-Aldrich). Organosulfates and nitrooxy organosulfates were identified from their characteristic MS
fragments (HSO₄⁻, SO₃²⁻ and neutral loss of HNO₃) and quantified using an organosulfate standard derived from β-pinene (MW 250) synthesized in-house and a surrogate standard of octyl sulphate (Sigma-Aldrich).

CONCLUSIONS

Figure 1 shows the annual variation in organosulfate and carboxylic acid concentrations at Station Nord in 2010 and at Zeppelin Mountain in 2008. At Station Nord a highly characteristic annual pattern in organosulfate and carboxylic acid occurrence is observed, with low concentrations of both classes of compounds during summer and fall (week 16 through 40) followed by a slight increase during the early winter months (week 44 and 48). In late winter and early spring a sudden increase in organosulfate and carboxylic acid concentrations is observed. During late winter and spring transport of air pollution from lower latitudes (especially Eurasia) into the Arctic is increases due to expansion of the polar air dome. This phenomenon is known as Arctic haze (Ottar, 1989; Iversen and Joranger, 1985; Flyger et al., 1980).

During the Arctic haze period at Station Nord it is recognized that OM peaks coinciding with the increased concentrations of organosulfates and carboxylic acids. Furthermore nss-sulfate, a tracer for long range transport, is also high in this period.

The annual concentration pattern of organosulfates and carboxylic acids is very different at Zeppelin Mountain compared to Station Nord. At Zeppelin Mountain almost constant concentration of organosulfates and carboxylic acids are observed throughout the year interrupted by four weeks of increased concentrations (week 7, 9, 13 and 17). All four weeks falls within the period of Arctic haze, and OM as well as nss-sulfate show concentration peaks in week 9, 13 and 17 as well, suggesting that the increased concentrations are caused by long range transport of polluted air into the Arctic.

Modelling of air mass transport using the HYSPLIT air mass back trajectory model (Draxier and Hess, 1998) revealed transport of air masses from Russia during all events of high concentrations both at Station Nord and Zeppelin Mountain. This observation agrees with previous measurements identifying Russia as an important contributor to Arctic haze (Rahn, 1981; Nguyen et al., 2013; Heidam et al., 2004; Heidam et al., 1999).

Interestingly the total concentration of organosulfates at Station Nord (47 ±14 ng/m³) and Zeppelin Mountain (28 ±6 ng/m³) during Arctic haze are much higher than observed in for example Denmark (≈ 1.1ng/m³) during spring and summer (Kristensen and Glasius, 2011). This concentration difference is especially due to the group of organosulfates with unknown precursors, which to our knowledge have not been observed before. The sources and precursors of these organosulfates as well as their occurrence in the Arctic atmosphere are very interesting and should be studied further.
Figure 1. Variation in total air concentration of observed carboxylic acid, organosulfates and nitrooxy organosulfates at Station Nord in 2010 and Zeppelin Mountain 2008. W is week number, A is anthropogenic, B is biogenic and U is unknown. On secondary axis: concentration of Organic Matter (OM) and non-sea-salt sulphate (nss-sulfate).

ACKNOWLEDGEMENTS

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MODELING BIOGENIC SECONDARY ORGANIC AEROSOL FORMATION IN THE SUBARCTIC

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Keywords: Secondary organic aerosol, α-pinene, ADCHEM, MALTE-BOX.

INTRODUCTION

Biogenic volatile organic carbon (BVOC) compounds, such as α-pinene, are emitted by the vegetation and oxidized in the atmosphere to form less volatile compounds. These compounds can take part in the formation and growth of secondary organic aerosols (SOA) and thus they can increase the aerosol load and also the concentration of cloud condensation nuclei which will affect climate.

We have modeled the formation and growth of secondary particles along an air mass trajectory over the northern European boreal forest and compared the results with size distribution measurements from three stations the air mass passes close to (Abisko, Pallas and Värriö).

METHODS

The model used is an updated version of the aerosol dynamic and particle phase chemistry module from the ADCHEM model (Roldin et al., 2011), coupled with the Master Chemical Mechanism version 3.2 (MCMv3.2) (Jenkin et al., 1997; Saunders et al., 2003). The emissions of BVOC (represented by α-pinene in our model) are estimated using a method described in Tunved et al. (2006). The model then considers the gas-to-particle partitioning of the 42 most important oxidation products. Liquid saturation vapor pressures of each oxidation product are decided by using the method proposed by Nannoolal et al. (2008).

RESULTS AND CONCLUSIONS

During the first 54 hours of the trajectory, the air mass is oriented over the Atlantic Ocean, whereas it spends the remaining hours over land where the particle mass starts increasing (see Figure 1). The modeled growth is mainly caused by organic gas-to-particle conversion and seems to be a bit slower than the measured growth. Despite this, the model seems to be able to handle SOA formation relatively well at realistic BVOC-emissions and low primary particle concentrations.

These are preliminary results which will be analyzed further and compared with results achieved by the model MALTE-BOX (Boy et al., 2013) which uses the University of Helsinki Multicomponent Aerosol model, UHMA (Korhonen et al., 2004). To test how well MCMv3.2 can describe the gas phase oxidation, a fully explicit gas phase oxidation scheme, called GECKO-A (Aumont et al., 2005), will also be applied. To further assess how different types of gas phase oxidation schemes perform, the semi-empirical two-dimensional volatility basis set (2D-VBS) suggested by Jimenez et al. (2009) will be implemented.
Figure 1. The solid line represents the total modeled particle volume along the trajectory, which consist mostly of SOA (dashed brown line) but also a small fraction of sulfate (dashed blue line). The modeled results are compared to size distribution measurements.

REFERENCES


Hygroscopic, CCN and volatility properties of submicron atmospheric aerosol in a boreal forest environment during the summer of 2010

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Keywords: hygroscopicity, CCN activity, volatility, κ, growth factor.

INTRODUCTION

Hygroscopic properties of atmospheric aerosol particles describe the interaction between the particles with ambient water molecules at both sub and supersaturated conditions in the atmosphere. Although the size of the particle is dominant factor (Dusek et al. 2006) determining whether a particle is a potential cloud condensation nuclei (CCN), hygroscopicity plays a role at the size close to the limit of activation (e.g. Roberts et al. 2002). For example atmospheric oxidation of particles can modify the hygroscopicity of the particles making them CCN active (Petäjä et al. 2006, Massoli et al. 2010, and Chang et al. 2010). Furthermore, hygroscopicity can give essential information on particle composition (Swietlicki et al. 2008).

RESULTS

A Volatility Hygroscopicity Tandem Differential Mobility Analyzer (VHTDMA) was used to measure the hygroscopicity and volatility of the ambient aerosols from 24 July to 07 August 2010 in Hyytiälä, Finland as a part of the HUMPPA-COPEC 2010 campaign. Several particle sizes were investigated, 50, 75 and 110 nm in more detail. In general the bigger the particle was the more hygroscopic it was. Black carbon had a little influence on hygroscopicity of aerosols of this study. The competition between the mass fraction of organics and SO₄²⁻ is probably the major contributor to the fluctuation of the hygroscopicity.

The CCNc-derived κ was slightly higher than the ones from HTDMA. This discrepancy has been observed before and it has to do with the fact that particulate organics have different solubilities in sub and supersaturated conditions, shown in Fig. 1. HTDMA measurements for larger particles should be performed to obtain better agreement between HTDMA-derived κ and the predicted κ (0.17) based on ZSR mixing rule.

The volatility properties obtained from the VHTDMA were compared with aerosol volatility behavior investigated using (VDMPS) during the studied period in Hyytiälä and during earlier years (Häkkinen et al., 2012), and they showed a good agreement with each other. Small particles evaporated more compared with large particles when heated. At temperatures above 200 °C, 80% of the aerosol material (by volume) was evaporated from the particles. However, there was still a significant amount of aerosol volume left at these high temperatures, see Fig. 2.

We studied the hygroscopicity of the particles after heating up to different temperatures. Particle hygroscopicity increased first when the heating temperature was increased to around 150 °C and decreased after 150 °C for 110 nm particles. This indicates that when heated up to 150 °C, the less hygroscopic aerosol material evaporated at lower temperatures than the more hygroscopic compounds. For 50 nm particles, the increasing and decreasing trends are not obvious. On the other hand, particles (50, 75 and 110 nm) were observed to have some hygroscopic material in them at all different heating temperatures. Comparing the hygroscopic growth factors from VHTDMA using V-mode and VH-mode, we could see that even at the highest heating temperature (280 °C) there was some hygroscopic material left, see Fig. 3. Since black carbon is hydrophobic this result supports recent studies that have found very low-volatile non-BC aerosol material in submicron ambient particles. This material can be e.g. organic salts or organic polymers from aerosol aging. We estimated the hygroscopicity of this “non-volatile” non-BC aerosol material for the three different sized particles. Due to simplicity of our approach the estimation gave too high hygroscopicities for the 50 nm and 75 nm particles. However, for the largest particles we
obtained reasonable hygroscopic growth factor of 1.17. In the future it would be important to obtain information about the hygroscopic properties of different low-volatile organics e.g. organic salts. This would help us to further interpret the VH-TDMA results we got and to understand better the chemical properties of submicron aerosol particles, most importantly particulate organics.

Figure 1: Calculated $\kappa$ values ($\kappa_{HTDMA}$ and $\kappa_{CCN}$) as a function of particle diameter using HTDMA measurements and CCNC measurements from this study and from study by Cerully et al. (2011).

Figure 2: Volume remaining fraction calculated from volatile growth factor ($\text{GF}_V$) obtained from the VTDMA measurements as a function of heating temperature for four different particle sizes.
Figure 3: Hygroscopic and volatile growth factors as a function of heating temperature obtained from the VHTDMA and the VTDMA of this study for 50 nm, 75 nm and 110 nm particles.

REFERENCES


The Arctic Ocean, once the domain of old, thick multiyear ice, is now largely covered by younger sea ice, much of it first-year ice. This transition affects many of the processes acting on the Arctic ice since first-year ice is thinner than and has many physical differences from multiyear ice. A clear example that affects the energy budget and resulting melt rate of the Arctic is that first-year ice generally has less topography, which leads to more extensive melt pond coverage. These ponds, underlain by thin ice, are dark, allowing much more sunlight to be absorbed by the ice or transmitted to the ocean than white ice, or even melt ponds on thicker ice. The transmitted light is absorbed by the ocean, providing an added source of turbulent heating from below.

To gain a better understanding of the energy budget of first-year sea ice in the high Arctic in summer, we observed the radiative and turbulent fluxes of energy both above and below an ice floe. The floe was typical for the region, between 82° and 82.5°N and 20° and 22.5°E, during the observation period of 26 July to 3 August 2012. Turbulent heat fluxes from the atmosphere to the surface and from the ocean to the underside were observed during the period at fixed locations 2 m above and 1 m below the ice. All components of the radiation budget were monitored continuously at one site. In addition, extensive surveys were carried out to measure the spatial variability of spectral and broadband albedo and spectral transmittance.

Combining the typical albedo and transmittance of various surface types from the transect data and a categorized aerial photograph of the floe, we were able to determine the floe-scale albedo and transmittance and combine this with the other fluxes to get an overview of the floe’s energy budget. The study area of approximately 0.4 km² was 96% ice covered, of which 77% was white (bare) ice, 16% was dark melt pond, and 7% was bright melt pond. The ice-covered area had an overall albedo of 0.47 and transmittance of 0.16, under the prevailing cloudy sky. Figure 1 shows that absorbed shortwave radiation (10–30 W m⁻² at midnight, 80–150 W m⁻² at noon) was generally the largest source of energy to the ice, though oceanic heat fluxes to the ice (−10 to +70 W m⁻²) were similar to, and in one case much larger than, nighttime solar heating. Atmospheric turbulent heating was negligible.

Average fluxes for the 7-day period are summarized in Table 1. Longwave emission worked to slightly offset the heating driven by solar absorption and oceanic turbulent heat transfer, but the net result was significant energy absorption by the ice, which drove ice melt at an average rate of about 3 cm day⁻¹.

The observations were made away from the continental slope, at depths greater than 3000 m, where Atlantic water inflow is unlikely to have contributed to the oceanic heat flux. It is therefore likely that the source of the oceanic heat was the transmitted solar radiation, which had resulted in a layer of warm water (0.3 to 0.4 K above local freezing temperature) between 10 and 30 m depth. During the observation period, fairly late in summer, the transmitted solar radiation was still about twice the oceanic heat flux, indicating this layer was continuing to accumulate heat. The heating of this near surface water layer
Figure 1. Time series of observed oceanic and atmospheric (sensible and latent) turbulent heat fluxes to the ice and net shortwave and longwave radiative fluxes. Also shown is the shortwave radiative flux absorbed by the ice and ponds in the ice-covered area (after removing the solar energy transmitted to the ocean). Turbulent fluxes are positive when they are providing heat to the ice; negative longwave fluxes indicate the ice is losing more heat to surface emission than it is gaining from atmospheric emission. All fluxes have been smoothed with a 2 h running mean. Totals are calculated for both the amount of energy absorbed by the ice (thick line) and by the ice-ocean system. In calculating the totals, missing atmospheric turbulent fluxes were assumed to be zero.

represents a potentially significant feedback resulting from the transition to thinner, first-year ice, which allows more sunlight to reach the ocean beneath. The higher transmittance provides for an oceanic heat source to melt ice from below, but the fact that much of it is stored in the layer also provides significant potential to delay autumn freezing.

<table>
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<tr>
<th></th>
<th>Average (W m⁻²)</th>
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</tr>
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</tr>
<tr>
<td>Total absorbed</td>
<td>64.8</td>
<td>100</td>
</tr>
<tr>
<td>Transmitted shortwave</td>
<td>26.0</td>
<td>–</td>
</tr>
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Table 1. Average of the Observed Fluxes Absorbed by the Ice and Ponds. The shortwave value excludes that which was reflected or transmitted. The values are also presented as relative contributions to the total energy absorbed by the ice and ponds during the period. The bottom line shows the solar energy transmitted through the ice and ponds to the underlying ocean water.

REFERENCE

MODEL STUDY OF THE IMPORTANCE OF CRIEGEE RADICAL CHEMISTRY FOR SULFURIC ACID FORMATION IN THE ATMOSPHERE

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Keywords: Atmospheric chemistry, modelling, CI radicals, sulfuric acid formation.

INTRODUCTION

As reported in numerous studies, sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) is a key component in aerosol formation and growth (Sihto et al., 2006; Weber et al., 1997). Aerosols affect climate and health and it is therefore of great importance to understand both the sink and source terms for sulfuric acid. However, model simulations have shown to underestimate the sulfuric acid concentration with up to a factor of two. Criegee intermediates (CI) are carbonyl oxides formed in the ozonolysis of alkenes. It is known that stabilized CI (sCI) can oxidize SO\textsubscript{2} to SO\textsubscript{3}, which can then further react with water to form H\textsubscript{2}SO\textsubscript{4}. However, the reaction rates reported in the literature for the oxidation of SO\textsubscript{2} by sCI span an order of magnitude of four and the effect of sCI on H\textsubscript{2}SO\textsubscript{4} formation has therefore yet to be quantified. Recent measurements of the oxidation of SO\textsubscript{2} by sCI show that these reactions are possibly substantially faster than previously thought. A model study by Boy et al. (2013) tested reaction rates for the sCI + SO\textsubscript{2} reactions reported by Mauldin et al. (2012) and Welz et al. (2012) for a time period of seven days. Boy et al. found that oxidation of SO\textsubscript{2} by sCI can be a crucial source of H\textsubscript{2}SO\textsubscript{4}, while other model studies have shown that the sCI reactions are not of great importance (Sarwar et al., 2013). In the present study we have tested the Criegee radical chemistry for a long-term period of 74 days using the zero-dimensional version of the model MALTE and data measured at the SMEAR II station in Hyytiälä, Finland.

METHODS

The simulations were performed with the 0-dimensional version of the model MALTE (Model to predict new Aerosol formation in the Lower Troposphere) described in detail elsewhere (Boy et al., 2006). Concentration measurements of monoterpenes, isoprene, OH and other inorganic trace gases as well as measurements of pressure, temperature and relative humidity (RH) were used as input for the model. Measurements were performed at the SMEAR II station in Hyytiälä (61°51’ N, 24°17’ E, 181 m a.s.l. (Hari and Kulmala, 2005)) as part of the 2007 EUCAARI project field campaign. Data available for the period of 24\textsuperscript{th} of May to the 6\textsuperscript{th} of July 2007 were used. Chemical reactions were selected from the Master Chemical Mechanism (MCM) v3.2 (Jenkin et al., 1997; Saunders et al., 2003) via website http://mcm.leeds.ac.uk/MCM and processed by the Kinetic Pre-Processor (KPP) (Damian et al., 2002). Various chemical scenarios were set up using the information gathered from an extensive literature search.
CONCLUSIONS

In Figure 1a, we show the measured and modelled sulfuric acid concentration using the reference chemistry from MCM. Figure 1b shows the measured and modelled sulfuric acid concentration after implementing the Criegee chemistry, and we see that there is no great improvement of the correlation between modelled and measured $\text{H}_2\text{SO}_4$. The model fit was improved quite drastically by using higher OH concentrations as input. The best fit was obtained by including the newest Criegee chemistry in combination with OH concentration input of three times the measured values, see Figure 1c.

![Figure 1a](image_a.png)

**Figure 1:** Measured and modelled sulfuric concentrations using a) MCM reference chemistry, b) MCM reference chemistry with increased reaction rates for the sCI reactions and c) MCM reference chemistry with increased reaction rates for the sCI reactions using an input OH concentration of three times the measured values.

This model study was performed using data from a boreal forest. Since monoterpenes are emitted
by boreal forests in large amounts, the sCI reactions are thought to be of particular importance in this setting. We found that the Criegee chemistry does not have a big impact on sulfuric acid formation, and that the Criegee chemistry is possibly not as important for atmospheric chemistry as believed.

ACKNOWLEDGEMENTS

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ANALYSIS OF INORGANIC IONS, CARBOXYLIC ACIDS AND ORGANOSULFATES IN PM$_{2.5}$ COLLECTED IN AARHUS, DENMARK – HIGHLIGHTS FROM WINTER 2012

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Keywords: Secondary organic aerosols, Inorganic ions, Organosulfates, UHPLC-MS, Ion Chromatography

INTRODUCTION

It is often difficult to observe evidence of (or against) the laboratory proposed formation pathways of secondary organic aerosol (SOA) compounds in ambient aerosol. Laboratory experiments have shown that inorganic acids affect SOA yields (Jang et al., 2002) and composition, e.g. through the formation of organosulfates (Surratt et al., 2007). In contrast, field studies have found little or no correlation between the acidic inorganic constituents and organic carbon concentrations (e.g. Tanner et al., 2009). In aerosol studies, it is thus important to quantify both inorganic and organic fractions, when accounting for the formation of SOA products, e.g. organosulfates, in the ambient air. In this study, aerosol samples were collected at an urban background location in Aarhus, Denmark for the analysis of inorganic ions, carboxylic acids, and organosulfates. Highlights from the inorganic analysis and preliminary results for carboxylic acids and organosulfates will be presented here. A more extensive analysis of carboxylic acids and organosulfates will be presented at the CRAICC 2013 annual meeting.

METHODS

Particles with aerodynamic diameter below 2.5 μm (PM$_{2.5}$) were collected as 12 h samples (6:00-18:00, 18:00-6:00 schedule) on quartz fiber filters using a high-volume sampler at the Department of Chemistry, Aarhus University during three winter weeks (23 Jan – 13 Feb, 2012). A circle punch (d = 28 mm) was stamped from each filter, extracted in water by sonication for 30 min and analyzed for major anions and cations using a Metrohm ion chromatograph (IC).

A quarter of each filter was extracted in 1:1 acetonitrile/methanol (v/v) by sonication for 30 min, evaporated to dryness by a gentle N$_2$-stream and redissolved in 10/0.1% acetonitrile/acetic acid (v/v) in water. The extracts were analyzed using ultra high performance liquid chromatography coupled through an electrospray inlet to a quadrupole time-of-flight mass spectrometer (UHPLC-ESI-qTOF-MS). The influence of air mass origin was evaluated from backward air parcel trajectories calculated for every 6 hours using the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model.

CONCLUSIONS

The major ionic constituents of urban PM$_{2.5}$ were measured in 41 samples representing a period of 21 days (Figure 1). The average ion concentration of the sampling period was 7.4 ± 3.5 μg/m$^3$. The major constituents were nitrate, sulfate, and ammonium with average atmospheric concentrations of 2.7 ± 1.6 μg/m$^3$, 2.4 ± 1.4 μg/m$^3$, and 1.7 ± 0.8 μg/m$^3$, respectively. The reasons for the variability of sample ion concentrations are not obvious, yet a sample series of low ion concentration is associated with air masses originating from east with relatively high wind velocities (cluster 3 in Figure 2), thus causing dilution and leaving less time for accumulation of PM$_{2.5}$ mass.
Figure 1. Concentrations of major ions (μg m⁻³) in PM₂.₅ samples collected in Arhus, Denmark during winter 2012. Numbered intervals refer to the HYSPLIT trajectories in Figure 2.

Figure 2. The HYSPLIT 10 m AGL mean 120 h back trajectories showing the 5 major clusters during the sampling period.

Preliminary SOA analysis has identified several anthropogenic and biogenic carboxylic acids, organosulfates (OS) and nitrooxy organosulfates (NOS). The identified organosulfates and nitrooxy organosulfates are listed in Table 1 with suggested structures and precursors. Organosulfates from α/β-pinene (OS250 – OS with molecular weight 250, NOS295, and NOS311) and limonene (NOS297) are observed in most samples. Additionally, organosulfates from precursors of both biogenic and anthropogenic origin (OS140, OS156, and OS170) are observed in most samples. OS and NOS from α/β-
pinene, isoprene, and limonene have previously been observed in wintertime aerosols at the same sampling site (Kristensen et al., 2012; Hansen et al., in preparation).

Table 1. Organosulfates and nitrooxy organosulfates identified in PM$_{2.5}$ samples collected in Arhus, Denmark during winter 2012.

<table>
<thead>
<tr>
<th>Measured m/z</th>
<th>Molecular formula</th>
<th>Proposed structure</th>
<th>Suggested precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>OS140</td>
<td>139.012</td>
<td>C$_3$H$_4$O$_3$S</td>
<td>glycolaldehyde$^a$</td>
</tr>
<tr>
<td>OS156</td>
<td>155.009</td>
<td>C$_2$H$_4$O$_6$S</td>
<td>glyoxal$^a$</td>
</tr>
<tr>
<td>OS170</td>
<td>168.986</td>
<td>C$_3$H$_6$O$_6$S</td>
<td>methylglyoxal$^a$</td>
</tr>
<tr>
<td>OS 250</td>
<td>249.073</td>
<td>C$<em>{10}$H$</em>{18}$O$_3$S</td>
<td>$\alpha$-$\beta$-pinene$^{a,b}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>More isomers</td>
<td></td>
</tr>
<tr>
<td>NOS295</td>
<td>294.070</td>
<td>C$<em>{10}$H$</em>{17}$NO$_3$S</td>
<td>$\alpha$-$\beta$-pinene$^{a,b}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>More isomers</td>
<td></td>
</tr>
<tr>
<td>NOS297</td>
<td>296.049</td>
<td>C$_3$H$_6$NO$_5$S</td>
<td>limonene$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>More isomers</td>
<td></td>
</tr>
<tr>
<td>NOS311</td>
<td>310.064</td>
<td>C$<em>{10}$H$</em>{17}$NO$_3$S</td>
<td>$\alpha$-$\beta$-pinene$^{a,b}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>More isomers</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Surratt et al., 2007. $^b$Surratt et al., 2008.

Aerosol (NH$_4$)$_2$SO$_4$ is a marker of aged sulfate particles (Harrison and Pio, 1983). A high correlation ($r^2 = 0.98$) between the molar concentrations of sulfate and non-nitrate-associated ammonium ([NH$_4^+$]-[NO$_3^-$]) along with a molar ratio of 1.97 show that the sulfate is almost entirely found as (NH$_4$)$_2$SO$_4$. This implies that the collected sulfate-containing particles on average are highly aged, and that significant long-range transport of particles has occurred during this winter period. Particle strong acidity [H$^+$], which is an estimate of the particle acidity, was calculated by means of charge balance. The average acidity of the particles, [H$^+$]$_{av}$ = -0.3 ± 2.1 nmol/m$^3$, show generally neutral particles during the sampling period. This finding suggests particle neutralization by gaseous NH$_3$ during atmospheric transport. However, evidence of acidic conditions is seen from chloride depletion, which is a result of reaction with gaseous acids, e.g. HNO$_3$ (Allen et al., 1989):

\[
\text{HNO}_3 (g) + \text{NaCl(s)} \rightarrow \text{NaNO}_3 (s) + \text{HCl(g)} \tag{1}
\]

Significant chloride depletion is observed for the sample series 28 Jan (N) – 1 Feb (N) (N = night) during a period of high wind velocity air mass trajectories from the east (cluster 3 in Figure 2). Chloride was below the detection limit for 28 Jan (N), while the [Cl]/[Na+] mole ratios for 29 Jan (D) – 1 Feb (N) (D = day) are in the range 0.41–0.91 (Figure 3), which is lower than the 1.17 ratio in sea-salt. Outside this
period a much more variable pattern of $[\text{Cl}^-]/[\text{Na}^+]$ ratios is observed, which is a result of the diverse sources of chloride, i.e. sea salt, road salting, and secondary chloride (e.g. from biomass burning). Assuming that all primary chloride is associated with sodium it is possible to account for the surplus chloride as secondary chloride. This is inferred from the good molar correlation ($r^2 = 0.82$) between excess ammonium (here defined as $[\text{NH}_4^+]$-($2[\text{SO}_4^{2-}]$+$[\text{NO}_3^-]$)) and surplus chloride ($[\text{Cl}^-]-[\text{Na}^+]$). It is thus concluded that the particles in the sample series 28 Jan (N) – 1 Feb (N) have been subjected to significant acidic conditions during their aging. This conclusion would not be reached by only accounting for sulfate, nitrate, and the acidity of the samples.

Tentative quantitative results for OS170, OS250, and NOS295 show good correlation between their concentrations and the sulfate concentration. However, there is no correlation between the concentration of OS-compounds and the $[\text{Cl}^-]/[\text{Na}^+]$ ratios. Additionally, good correlation between the concentration of OS-compounds and phthalic acid is observed, although OS250 and NOS295 do not have sources in common with phthalic acid. Phthalic acid is a marker of anthropogenic emissions (Kleindienst et al., 2012), thus the correlation is indicative of anthropogenic enhancement of biogenic SOA production. The tentative organosulfate results indicate that the fluctuations in concentration observed in this study are not caused by acidity differences but rather correlates with anthropogenic emissions.

![Figure 3](image-url)

Figure 3. $[\text{Cl}^-]/[\text{Na}^+]$ mole ratios of PM$_{2.5}$ samples collected in Arhus, Denmark during winter 2012.

The results show that the complex atmospheric system complicates the search for evidence in ambient environment of the proposed reaction pathways of organosulfates and evidence of acid-catalyzed SOA enhancement.

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aerosols—speciation, annual variation, and concentration levels.


MODELING LATENT HEAT EXCHANGE IN BOREAL AND ARCTIC BIOMES

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Keywords: LATENT HEAT FLUX, EDDY COVARIANCE, PENMAN-MONTEITH, STOMATAL RESISTANCE, AERODYNAMIC RESISTANCE

ABSTRACT

Boreal and arctic ecosystems cover almost 25\% of the surface area of the globe and are sensitive to the potential effects of the climate change. The most of the intensive work concerning the eddy covariance tower network during the past decades has concentrated to study the fluxes of carbon dioxide while only few large scale intensive latent heat flux and evapotranspiration studies have been done. Evapotranspiration from the vegetation surfaces is, in most cases, largely regulated by the stomata of the forest trees or other vegetation.

The Penman-Monteith equation (PM) is probably the most used approach that has been used in the estimation of crop evapotranspiration (Penman 1948, Allen 1998). In the simplest approaches the component of aerodynamic resistance is expected to be constant (mean wind speed 2 m s\textsuperscript{-1}) and many studies have used successfully different simplified formulations of PM. However, in biological systems the annual biological dynamics of the system will determine the rates of evapotranspiration.

In this study we introduce a new approach that is taking into account the delayed stomatal spring recovery that has been observed in studies concerning the photosynthesis (Gea et al 2010, Mäkelä et al 2004). We modeled latent heat flux parameters based on the data that is collected from the boreal and arctic eddy covariance stations. The calibration of the model was done in order to produce site-specific parameters and also for different ecosystem types. This information is valuable for estimating how vegetation specific latent heat flux might change in the warming climate.

METHODS

Site data for the model calibration were collected from the different Fluxnet database (European Fluxes Database Cluster \url{http://gaia.agraria.unitus.it}, Fluxnet Canada \url{http://fluxnet.ornl.gov/site_list/Country/CA}, Ameriflux \url{http://ameriflux.ornl.gov}, and Asiaflux \url{http://www.asiaflux.net}). The selected eddy covariance (EC) sites were representative for hemi-boreal, boreal and arctic conditions and covered the most common ecosystem types. Agricultural ecosystems were excluded from the analysis. The sites were grouped based on the dominant plant type and time since disturbance into 9 different categories. These were: cut or burnt areas temporary void of trees (C), Douglas fir forests (D), pine forests (P), spruce or fir dominated forests (S), deciduous forests (Le), larch forests (La), wetlands (W) and tundra (T). We attempted to select all sites in the boreal and hemi-boreal region but we finally rejected sites with short time series, with measurements only during summer and with large gaps in the data. We acknowledge that this rejection process was partly subjective. Our quality requirements were stricter for ecosystem types
that are well represented in the database while we had less stringent requirements for vegetation types that were not often measured.

Figure 1. Site location and distribution of eddy covariance sites used in the modeling.

DATA QUALITY CONTROL AND GAP-FILLING

Over 400 EC years were pre-checked and quality controlled concerning the meteorological variables and latent heat flux (λE) required for the estimation. We required rather complete time series of eight meteorological variables: air temperature (Ta), wind speed (WS), global radiation (Rg), net radiation (Rn) and air pressure (Pa) and water vapor deficit. Relative humidity (RH) was used to calculate saturation vapor pressure (VPD) if it was not provided in the original data.

The model parameter estimation used (sometimes but rarely gap-filled) meteorological variables provided by the data owners were used. However, parameter estimation was always using non-gap-filled measured λE fluxes. Small gaps (a few hours) in recorded air temperature data were linearly interpolated. For some stations longer gaps in air temperature and VPD were calculated from data recorded at the nearest weather station.

LATENT HEAT FLUX MODEL

We estimated evapotranspiration using the Penman-Monteith equation (as presented by Monteith 1948):

\[
\lambda E = \frac{Rn + \rho_a c_p \delta s \epsilon_a^{-1}}{\Delta + \gamma (r_s + r_a) r_a^{-1}}
\]

Where, \(\lambda E\) is the latent heat flux (W m\(^{-2}\)), \(R_n\) is the net radiation (W m\(^{-2}\)), \(\rho_a\) the dry air density (kg m\(^{-3}\)), \(c_p\) the specific heat capacity of air (J kg\(^{-1}\) K\(^{-1}\)), \(\delta_s\) is vapor pressure deficit (Pa), \(\Delta\) is the rate of change of saturation specific humidity with air temperature (Pa K\(^{-1}\)) and \(\gamma\) is psychrometric constant (\(\gamma \approx 66\) Pa K\(^{-1}\)), \(r_s\) is the stomatal resistance (s m\(^{-1}\)) (referred also as surface resistance). Atmospheric resistance \(r_a\) (s m\(^{-1}\)) (referred also as aerodynamic resistance) was calculate from the EC data according to
2) \[ r_a = \frac{U}{u_*^2} + \frac{kB^{-1}}{ku_*} \]

where \( U \) is wind speed (m s\(^{-1}\)), \( u_* \) is friction velocity (m s\(^{-1}\)), \( k \) is the von Karman constant (dimensionless). The excess resistance parameter \( B^{-1} \) was set to the value of 2 (dimensionless) in order to estimate the aerodynamic resistance in a similar way for all sites. The used value is suggested to be representative for forest (Launiainen 2010, Verma 1989) and has been used also for other vegetation types. \( kB^{-1} \) might vary between vegetation types as well as seasonally (Kustas et al 1989). However, in simulations the effect of this element in relation to total aerodynamic resistance is small and we assume that used parameterization does not have a significant role in the calculations related to \( r_a \).

The stomatal resistance was estimated using a multiplicative model.

3) \[ r_s = f(P) f(\delta_e) f(R_D) \]

Based on the works of Mäkelä et al. (2004) and Gea-Izquierdo et al. (2010), we assume that there is a change in stomatal resistance \( S(t) \) within the year as a function temperature, with the following functions:

4) \[ S(t) = \min\left(\frac{\int_{T_{\text{slow}}}^{T(t)} \frac{dt}{\tau}, 1} \right) \]

where, \( T \) is air temperature , \( \theta \) is the average temperature below which there is slow/delayed response of stomatal resistance to temperature, \( \tau \) is the delay of stomatal response in days.

The phenological development of stomatal resistance \( f(P) \) was described as:

5) \[ f(P) = r_{s\text{Max}} - 2(r_{s\text{Max}} - r_{s\text{Min}})(1 - \frac{1}{1+\delta}) \]

where, \( r_{s\text{Max}} \) and \( r_{s\text{Min}} \) are the modeled maximum and minimum stomatal resistance (s m\(^{-1}\)), \( k_r \) is stomatal response to global radiation (W m\(^{-2}\)) and \( k_{vpd} \) is the stomatal sensitivity to VPD slope (Pa).

We estimated the stomatal resistance based on ideas of Wong et al. (1979) and Leuning (1995) that assume a linear relationship between stomatal conductance and the rate of photosynthesis:

6) \[ f(R_g) = \frac{k_R R_g}{(R_g + 5)} \]

Where \( k_R \) is a parameter and \( R_g \) the global radiation

and

7) \[ f(\delta_e) = (1 + \frac{\delta_e}{k_{vpd}}) \]

STATISTICAL ANALYSIS

The modeling was implemented in R software (R-core team 2013) by using non-linear least squares regression (the nls-function of the stat library using the nl2sol algorithm)). The parameter \( \theta \)
and $\tau$, linked to the phenology of transpiration, were estimated, however, iteratively using a grid with a density of 1 days ($\tau$) and 1 degree Celsius ($\theta$). For rare cases where the use of the phenology model improved the fit of the model by less than 2%, $\theta$ and $\tau$ were set as constants ($\theta=5$ degrees C and $\tau=2$ days).

Parameter estimation was done using half hourly values. We provide two different parameter estimates. Firstly we estimated parameter values for each site separately and secondly we pooled our data for each functional type and estimated the parameters for each ecosystem type. We use a pseudo $R^2$ (also called proportion of explained variance here after considered as PR$^2$) often called proportion of explained variance to measure the goodness of fit of our models. It is defined as:

\[
PR = 1 - \frac{\sum(y-y\hat{y})^2}{\sum(y-y_bar)^2}
\]

where, $y$ is the measured value of the variable in question, $y\hat{y}$ is its predicted value and $y_bar$ its measured values. PR$^2$ is the pseudo $R^2$. For a linear regression this would give the same values as the traditional $R^2$.

RESULTS & DISCUSSION

The annual average air temperature (as calculated from the climatological data) was lowest for Tundra sites and highest for Douglas fir varying almost 20 C from -10 to +8 C. Extremely continental sites, Yakutsk Larch & Pine sites (RU-Ylr & RU-Ypf) had also very low annual mean temperatures (-10 C (data not shown).

Concerning the S and $\tau$ factors the mean air temperature threshold to reach minimum stomatal resistances were lower for wet- and tundra-type sites and the values of $\tau$ smaller than for forested sites. For forests the threshold temperature varied from 10 to 13 C and $\tau$ from 15 to 25 days (Fig 2 a & b). The longest adaptation period and highest saturation temperature were observed for grass-type vegetation. Douglas fir did not show any seasonal phenological pattern for stomatal conductance and there were no clear values for $\tau$. 
Figure 2. Distribution of model parameters $r_{\text{Max}}$ (a), $r_{\text{summer}}$ (b) $k_{\text{rd}}$ (c) and $k_{\text{vpd}}$ (d). Results are presented according to biome types: C: cut / open / burned originally forested sites, D: Douglas Fir, G: Grassland, La: Larch, Le: Deciduous Broadleaf forest, P: Pine, S: Spruce, T: Tundra, W: wetland. Red points are model parameters that are calibrated against the all ecosystem-specific data and represents universal values that can be used in the modeling.

FIT OF THE MODEL

Squared pseudo correlation $R^2$ values for half hourly data varied from 0.4 to 0.84. The mean $R^2$ value was 0.65 (± 0.1 (mean ± sd)). When we estimated the model for average daily evapotranspiration values the $R^2$ varied from 0.48 to 0.92 with a mean of 0.77 (± 0.1) (RU-Cok, CA-NS5) and for monthly evapotranspiration estimates $R^2$ values varied between 0.58 to 0.99 with a mean 0.90 (± 0.07) (RU-Cok, RU-Ha1) (Figure 3).

When all data from each land cover types were pooled and estimated together, biome specific $R^2$ was slightly lower for all vegetation types for 0.5 h data than the arithmetic mean based on site-wise estimation. However, for daily and monthly time span, the biome specific $R^2$ were slightly higher.
than the mean of site-wise calculated estimated data, except for tundra sites (Figure 3). Estimated and measured daily means for $\lambda E$ exchange were highly correlated and PR$^2$ varied from 0.84 to 0.98 (Fig 3).

Figure 3. Pseudo correlation coefficients for 0.5 h (A), daily (B) and monthly (C) model fits. Results are presented according to vegetation types: C: cutted/open canopy, D: Douglas Fir, G: Grassland, La: Larch, Le: Leaf, P: Pine, S: Spruce, T: Tundra, W: wetland. Red points are correlation coefficients for the pooled data.

VEGETATION DIFFERENCES IN $\lambda E$

In order to investigate differences between vegetation type, $\lambda E$ flux for different land cover types were modeled based on meteorological data and ecosystem calibrated model parameters in daily scale. Predicted $\lambda E$ flux for daytime (from 9:00 to 17:00) where highest for deciduous broadleaf forest and lowest for tundra and Douglas fir. We did not observe any major differences between daily and annual $\lambda E$ flux behavior (Fig 4 & 5) when simulations were done based on the meteorological data of Hyytiälä (FI-Hyy 2011).

Figure 4. Predicted $\lambda E$ flux based on bulk meteorological variables recorded at Smear II station (FI-Hyy) 29.6.2011. $\lambda E$ flux is calculated for the daytime from am 9:00 to 17:00 pm.
The $\lambda E$ flux from the vegetated surfaces is regulated by the aerodynamic and stomatal resistance. Based on the simulation with bulk meteorological data (fig 4 & 5) shows that $\lambda E$ values under identical meteorological conditions differ depending on the vegetation type. One reason for these differences is that the proportion of stomatal resistance of the canopy resistance varies (Fig 6). These results suggest that stomatal control is mainly controlling the $\lambda E$ in Larch, Leaf, Pine and Spruce while in some other ecosystems the role of $ra$ can be significant.

Figure 5. Proportion of $\lambda E$ (%) from the annual net radiation (NetRad) based on the universal vegetation specific model parameters.

Figure 6. The proportion of stomatal resistance from the total canopy resistance ($Rs/(Ra+Rs)*100$). Bars represent the variation range and proportion (%) of $r_s$ from $r_c$ based on daily pooled data.
CONCLUSIONS

The key findings of this study are the seasonal behavior of stomatal conductance and the differences of phenology between ecosystems type govern the land surface in the boreal and artic biomes. In general the site-specific fits were good and for most sites and ecosystem types the universal parameterization of the model introduced fair estimates related to $\lambda E$ flux between land surface and atmosphere. The fit of the generalized parameterization was lower than for the other ecosystem types that might be caused by the fact that the model does not take into account ground heat flux or the energy that is used to melt the frozen surface layer in arctic stations. Further on, the over estimation of the flux for some sites might be caused by the drought and limited water availability.

Our results could be used in later in the research topics related to Earth system and hydrological modeling.

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MEASURING THE CONTRIBUTION OF SHIP TRANSPORT TO PARTICLE NUMBER AND VOLUME CONCENTRATIONS

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Keywords: Ship traffic, Particle number, Particle volume, SMPS.

INTRODUCTION

There is limited atmospheric field data on the number and mass concentration contributions from ship traffic in aged ship plumes as function of particle diameter. Studies of the size-resolved number concentration of ship plumes with an age of a few minutes are available in limited number (Petzold et al., 2008; Jonsson et al., 2011). However, data on size resolved mass emissions and data on plumes aged for a longer time do not exist altogether. Hence, modelling to what extent ship particles contribute to the radiative forcing and to the population exposure for different aerosol particle size fractions is problematic for plumes aged on longer time scales, since there is no data to validate with.

Basically, there are two ways how to quantify ship contributions using measurement data: 1. To perform measurements of aged ship plumes, and 2. To perform source/receptor modelling at inland locations where there is a need to quantify exposure to different particle sources. In this study, particle number size distribution measurements of approximately 1-hour aged ship plumes in the North Sea have been performed. In lack of other data from other parts of the world, this data is intended also to be extrapolated to other parts of the world, for example the Arctic, where emissions from ships are believed to cause future problems with the opening of the Arctic sea ice in summer.

MEASUREMENTS AND DATA

To characterize ship emissions in the North Sea, measurements were performed at the coastline of Danish peninsula Jutland, at the wind power test facility station Høvsøre (56°26′39″N ; 8°09′06″E) (Figure 1). The station is placed roughly 15-50 km from one of the largest ship lanes in Denmark, which means that ship plumes from this ship lane are arriving approximately after 1 hour to the station depending on the wind speed from WNW. The particle number size distribution was measured using a TSI 3080 SMPS system (Wang and Flagan 1990). Before entering the SMPS system, the aerosol particles were dried to between 5 and 40 % relative humidity using a naphion type drier. The aerosol and sheath flow rates in the SMPS were 1.0 and 5.0 l/m respectively, and the sampling time was 255 s, which yielded a size distribution in the size range of 12.0 to 505 nm electric mobility diameter each 5 minutes. Losses in the naphion drier were accounted for, and these amounted to maximum about 50% at 12 nm diameter.
METHODS

We divided the days of the measurement data into 5 categories depending of the paths the air arrives to Høvsøre. We did this based on 2-day HYSPLIT back-trajectories ending at 100m altitude for every hour of the day (Draxler, 1999). The categories and their representative fraction of days are shown in Table 1. For a day to be classified as ship day all trajectories of the day have to cross the ship line (the line between 6°30' E, 56°15' N and 8°00' E, 57°18’ N, Figure 1) within three hours before arriving to Høvsøre. Also other sea day and inland day require all trajectories to come from sea or inland, respectively. If there were less than 20 trajectories for a day, the day was classified as missing data day regardless of where the air was coming from.

<table>
<thead>
<tr>
<th>Day type</th>
<th>Number of days</th>
<th>Fraction of days (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ship day</td>
<td>39</td>
<td>28.5</td>
</tr>
<tr>
<td>Other sea day</td>
<td>17</td>
<td>12.4</td>
</tr>
<tr>
<td>Inland day</td>
<td>16</td>
<td>11.7</td>
</tr>
<tr>
<td>Mixed day</td>
<td>63</td>
<td>46.0</td>
</tr>
<tr>
<td>Missing data day</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Total</td>
<td>137</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 1. Classification of measurement days into different categories.

In the aerosol particle number concentration there were clear short-time peaks in the data during most ship days, but not during other sea days or inland days (Figure 2). The aerosol size distribution during these periods peaked at 35-50 nm, indicating recent emissions. As there are no other periodical emissions sources nearby, we assume these peaks to be caused by the plumes of the ships passing upwind of the station at the ship lane.

Separating the peaks from background particle concentration was not straight forward. We did not have direct measurements of the same air masses before their arrival to the ship lane, and we could not use any
default marine particle scheme since the air masses often passed other ship lanes, oil production area or continental sources before arriving to the nearest ship lane. Therefore we defined the background (Nb) as running 25 percentile of the particle number concentration data with operating window of 40 consecutive measurement cycles (about 3.5 hours) (Figure 2). This allowed us to separate the peak and background conditions from each other, but it also creates artificial peaks during periods when background is changing rapidly. Such periods were removed from the analysis. In the following analysis the difference between measured and background particle number concentrations is called excess particle number concentration (Ne), and the ratio of measured to background particle number concentrations is called excess number concentration ratio (RNe). We replaced negative numbers in Ne and Re with very low values in order to avoid problems when using logarithmic operators later in the data analysis.

We also calculated the background volume concentration between 12-150 nm and between 12-300 nm in the same way as for the number concentration. In this we assumed all particles to be spherical and to have the geometric mean diameter of the corresponding SMPS size bin. We then calculated the excess volume concentrations (Ve150 and Ve300) as well as the excess volume concentration ratios (RVe150 and RVe300). Most of the particle volume is formed by the particles near the upper diameter limits of the ranges given above. That, combined with the low number of particles and therefore poor counting statistics in these sizes made especially Ve300 and RVe300 more uncertain than the corresponding number based values.

We defined a plume peak to be a period where either one of the following criteria is met: 1) The excess particle number concentration (Ne) exceeds 1000 cm^-3 or 2) The excess number concentration ratio (RNe) exceeds 2.0. Our definition of a plume peak excludes random noise from the plume peak analysis, but it also excludes smaller peaks, especially during periods of high background particle number concentration (Figure 2).

![Figure 2](image.png)

**Figure 2.** Left: Measured particle number-size distribution during a ship-day, and the separation of background particle number concentration. Right: Excess particle size distribution, excess particle number concentration (Ne) and excess concentration ratio (RNe) during plume peak periods.

We analysed every individual plume peak in our data for maximum Ne, as well as Nb and RNe at the same time point. We also classified the plume peaks according to their type (whether the plume peak is...
included because of criterion 1 or 2, or if the plume consists of several peaks in Ne data). We also calculated the duration how long the plume peak criteria are met for each plume peak in the Ne and Re data, and the total number and volumes of excess particles during that time range. Finally we calculated the average measured particle number-size distribution and particle volume size distribution during each plume peak, smoothed them with running average (operating window of 3 consecutive size bins) and extracted the number- and volume based peak diameters of the size distributions for each plume peak.

We estimated the average contribution of ship traffic to the daily number (and volume) of particles at Høvsøre during ship days. This was done using two different approaches. The first approach was to divide the daily sum of excess particle number (or volume) concentration by the daily sum of all measured particles. This approach over-estimates the ship contribution, since it includes the positive part of the noise in Ne (or Ve) and excess particles created by small changes in the background concentrations in the ship plume fraction. The second approach was to sum up the number (or volume) of excess particles in each plume, and to divide that by the daily sum of all measured particles. This approach underestimates the ship contribution, since it does not include smaller ship plumes that do not fill either one of the plume peak criteria, and it also leaves out the beginning and end of each plume where the plume peak criteria are not met.

RESULTS

During ship days (when the air mass was coming over the ship lane) the number of ship plumes per day varied between 0 and 30 with an average of 9.3 plumes per day. Approximately half of the plumes were single plumes with Ne peaking above 1000 cm$^{-3}$. The rest were divided roughly equally between single plumes with Ne below 1000 cm$^{-3}$ (included because of the second criterion only) and plumes with multiple peaks in Ne. The average plume duration was 11 minutes corresponding to slightly over two measurement cycles. The plumes covered on average 8.6% (range 0 - 38%) of the total time of the day.

The number of excess particles during a plume varied from 100 to 22900 particles cm$^{-3}$ with average of 3100 cm$^{-3}$ per plume. The corresponding volumes between 12 and 150 nm were 0.0008 to 0.50 μm$^3$ cm$^{-3}$ with average of 0.09 μm$^3$ cm$^{-3}$. Most of the plumes were close to the smaller edge of the particle number range indicating that there are also a lot of smaller plumes which are excluded from our analysis. The number of plume particles per day and number of plumes per day were proportional to the background particle number concentration level during the same day. Higher background indicated more plumes. The number of particles per plume showed no clear dependence to the background level. This does not mean that the plumes are of same strength during different days, but rather that when the background particle levels are low, only the strongest plumes are included in our analysis. We assume that during low background days both plumes and background are diluted due to mixing with cleaner air.

The peak diameters of the plume excess particle number concentration were typically (25 and 75 percentile) between 36 and 48 nm with average 41 nm (figure 3). These were slightly larger than in the few-minutes old plumes measured by Jonsson et al. (2011) at Gothenburg harbour, indicating that the plume particles grow by condensation and coagulation during the first hours after emission. Peak diameter histogram of the excess volume size distribution (12-150 nm) was two-modal. This is partly due to another mode of larger 100-200 nm particles that can be observed in some plumes, but it is also partly caused by the poorer counting statistics and larger relative noise in the larger diameter bins. Peak diameter in the excess volume concentration between 12 and 300 nm was mostly on the upper edge of the diameter range indicating a strong counting statistics effect.
During ship days, the contribution to total number and volume concentrations was estimated. Using the method that underestimates the contributions, yields average values of 9.1 %, 7.1 %, and 2.6 % for the number contribution, and the volume contributions between 12 and 150 nm diameter and the volume contribution between 12 and 300 nm diameter respectively. Using the method that overestimates the contribution, the following values were derived: 20.1 %, 18.6 % and 11.8 % respectively. This yields a range of values for the contribution of one ship lane to particle concentrations approximately 1 hour downwind of the ship emissions according to Table 2. The values can also be extrapolated to the entire year, including also the days when we have no winds from the ship lane to get a measure of how important the ship plume is in total, see Table 2. These values have been calculated assuming mixed days give half of the contribution of ship days.

<table>
<thead>
<tr>
<th>Concentration measure</th>
<th>Contribution during ship days</th>
<th>Contribution during entire year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>9.1 – 20.1 %</td>
<td>4.8 – 10.5 %</td>
</tr>
<tr>
<td>Volume (12-150 nm)</td>
<td>7.1 – 18.6 %</td>
<td>3.7 – 9.7 %</td>
</tr>
<tr>
<td>Volume (12-300 nm)</td>
<td>2.6 – 11.8 %</td>
<td>1.36 – 6.2 %</td>
</tr>
</tbody>
</table>

Table 2. Contribution from the North Sea ship lane to particle concentrations at Høvsøre.

DISCUSSION AND CONCLUSIONS

As can be seen in Table 2, the ship route in the North Sea has a significant effect on the particle number and volume concentrations at the coast line of Høvsøre, even if the contribution is extrapolated to the entire year including also those days when there is no wind from the current ship lane. It should be remembered also that this range of contribution from ship traffic calculated here is only valid for one single ship lane. The other ship lanes in the North Sea, and the other ship lanes in Danish sea waters might also provide a contribution, and could increase the contribution from ship traffic in general compared to what is shown in Table 2.

The study shows that the method is working in a sufficient manner for particle number concentrations at Høvsøre. For the peak plume concentration magnitude, there is a strong dependence on meteorology. In the relative contribution the meteorology effect is not as pronounced, as the plumes and background depend on meteorological conditions roughly in the same way.

Our data was not optimal for estimating the ship traffic contribution to particulate volume, especially outside the size region where most of the plume particles are located. The method itself is suitable for volume estimations, but for that one should use an instrument that measures volume or mass, not number.

The method should work better for Arctic environments since the background contribution is weaker, and the relative contribution from ship plumes should also be higher.
ACKNOWLEDGEMENTS

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Desorption and incorporation kinetics of D$_2$O in a precursor state on ice between 170-200 K

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Keywords: DESORPTION, WATER ACCOMMODATION, KINETICS, ENVIRONMENTAL MOLECULAR BEAM, CIRRUS, ICE

INTRODUCTION

Water exchange between its three states of aggregation is of central importance for the Earth system. The rate of water condensation and evaporation on atmospheric ice particles influences the lifetime and properties of clouds, and thereby affects radiative forcing, precipitation and climate. However, the current picture of water uptake on ice is far from clear and measurements of the efficiency of water accommodation on ice somewhat mysteriously vary by more than two orders of magnitude. In earlier papers [1-5], we reported a newly developed environmental molecular beam (EMB) method by which the temperature of a probed ice surface can be set at a point relevant to upper tropospheric conditions. Here we attempt to directly determine the desorption kinetics of water molecules from pure water ice surfaces between 170 K and 200 K. We discuss the existing experimental results in detail and present a kinetic model that captures the observed trends.

METHODS

Experiments were performed using an ultra-high vacuum (UHV) environmental molecular beam (EMB) apparatus [1, 2] that focuses a low density beam of molecules onto a surface. The surface is housed within an environmental chamber that allows finite vapour pressures (< $10^{-2}$ mbar) to be sustained. Thus stable H$_2$O ice layers in dynamic equilibrium with water vapour are condensed onto a substrate. The technique differs critically from other molecular
beam systems in that it allows surfaces under atmospherically relevant temperatures and pressures to be directly probed. Kinetic information is collected by analysing molecules desorbing from the surface using a rotatable quadrupole mass spectrometer (QMS). The incident beam is a combination of He and D$_2$O gases that allows for monitoring of surface coverage with elastic He scattering while water uptake is simultaneously directly measured. The reflections of a 670 nm laser from the surface are also monitored to measure ice thickness. The molecular flux from the sample surface is measured using the QMS and ion counts are recorded as a function of time. The distributions of recorded measurements are converted into time-of-flight (TOF) measurements and fit in a non-linear least squares manner for the thermal desorption [3-5].

RESULTS

We have investigated the kinetics for water uptake and desorption from pure ice surfaces at temperatures from 170 K to 200 K. Using a kinetic model, we are able to separate and quantitatively determine the competitive desorption and incorporation processes of D$_2$O molecules in a precursor state. The two processes both follow first order kinetics, where desorption rate coefficients are in the 8-117 s$^{-1}$ range, and the incorporation rate coefficients lay between 25 and 99 s$^{-1}$. The Arrhenius pre-exponential factor $A = 1 \times 10^{10 \pm 5}$ s$^{-1}$ and activation energy $E_a = 0.34 \pm 0.09$ eV are determined for evaporation, and for incorporation $A' = 1 \times 10^{5 \pm 1}$ s$^{-1}$ and $E_b = 0.13 \pm 0.06$ eV. Accommodation coefficients are calculated by the ratio of incorporation to total water flux, yielding results from almost unity at low $T$ and decreasing with increasing temperature reaching $0.41 \pm 0.20$ at 200 K. Using a precursor model the results for desorption rate, incorporation rate and accommodation coefficient can be extrapolated to a wider temperature range. Possible errors and uncertainty are discussed and results from earlier studies are summarized and compared to the present results.

IMPLICATIONS

This study contributes to a detailed understanding of precursor states on surfaces by combining experimental results from the EMB technique and a kinetic precursor model. The approach can be used to characterize many systems, and the determination of accommodation coefficients complements other studies. Future work should focus on temperatures above 200 K for two reasons. Firstly, above 200 K the accommodation coefficient appears to reach values below 0.1, which is low enough to influence particle growth processes in cloud
models. Secondly, the validity of the irreversible precursor model used here should be tested at high temperatures.

ACKNOWLEDGEMENTS

This work was supported by the Swedish Research Council and CRAICC. PP thanks the Wenner-Gren Foundation for providing funding for an extended stay at the University of Gothenburg.

REFERENCES

DISTRIBUTION OF ORGANIC ACIDS AND ORGANOSULFATES IN SOA IN NORDIC REGIONS DURING SUMMER 2009

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Keywords: Organosulfates, Carboxylic acids, Monoterpen, Isoprene, HPLC-MS

INTRODUCTION

Secondary organic aerosol (SOA) accounts for a significant fraction of ambient tropospheric aerosols. The aerosols are known to participate in chemical and physical reactions and transformations in the atmosphere and potentially influence the climate (Hallquist et al., 2009). The oxidation of monoterpenes by hydroxyl radical (OH) or ozone contributes to the formation of biogenic secondary organic aerosol (BSOA) such as multifunctional organic acids; e.g. cis-pinic acid and pinonic acid. First-generation oxidation products such as pinonic acid originating from α-pinene may be further oxidized in the atmosphere by OH to give the second-generation oxidation product 3-methyl-1,2,3-butane tricarboxylic acid (MBTCA) (Szmigielski et al., 2007). In addition, anthropogenic SOA such as adipic acid, benzoic acid and phthalic acid originating from the oxidation of cycloheptene, toluene and xylene may also contribute to the total SOA and may be used as tracers for anthropogenic pollution. Organosulfates and nitrooxy organosulfates of isoprene and monoterpenes have been identified as products of acid-catalyzed uptake of their VOC precursors in the aerosol phase (e.g. Surratt et al., 2007; Inuma et al., 2007). Organosulfates and nitrooxy organosulfates are formed by processes involving both biogenic and anthropogenic emissions, and can thus be regarded as tracers of ageing of aerosols in mixed air masses.

METHODS

PM₁₀ filter samples were collected at four Nordic rural background sites during the SONORA (Secondary Organic aerosol in the NOrdic RurAl Environment) sampling campaign (Figure 1, Table 1). All sites are representative for various environmental types encountered in Northern Europe. The samples were collected weekly from August 5th to September 9th 2009. After extraction, the samples were analysed by High Performance Liquid Chromatography (HPLC) coupled through an electrospray inlet to a quadrupol time-of-flight mass spectrometer (qTOF-MS). Carboxylic acids were identified and quantified by the use of authentic standards. Organosulfates and nitrooxy-organosulfates were identified from their characteristic MS-fragments (HSO₄⁻, SO₃⁻ and HNO₃⁻) and the isotopic patterns of sulphur and nitrogen and quantified by the use of surrogate standards. Organic carbon (OC) was quantified using thermal-optical instrument from Sunset laboratories Inc. and OC/EC Thermal Optical Carbon Analyzer from DRI (Desert Research Institute) (Yttri et al., 2011)
Table 1. Location of the four Nordic sites participating in the SONORA sampling campaign and the duration of the sampling period

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>Location</th>
<th>Height (m.a.s.l)</th>
<th>Sampling period</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birkenes (Norway)</td>
<td>58º23'N, 8º15'E</td>
<td>190</td>
<td>05.08.2009–02.09.2009</td>
<td>Rural background</td>
</tr>
<tr>
<td>Hyytiälä (Finland)</td>
<td>61º51'N, 24º17'E</td>
<td>181</td>
<td>12.08.2009–09.09.2009</td>
<td>Rural background</td>
</tr>
<tr>
<td>Lille Valby (Denmark)</td>
<td>55º41'N, 12º08'E</td>
<td>10</td>
<td>05.08.2009–02.09.2009</td>
<td>Semi-rural background</td>
</tr>
<tr>
<td>Vavihill (Sweden)</td>
<td>56º01'N, 13º09'E</td>
<td>172</td>
<td>05.08.2009–02.09.2009</td>
<td>Semi-rural background</td>
</tr>
</tbody>
</table>

At all four sites, biogenic secondary organic aerosol showed to be the single most important source (48–57 %) of carbonaceous aerosol originating from natural sources (Yttri et al., 2011).

Using HPLC-MS, a total of eight carboxylic acids were identified in the aerosol samples collected from the four locations: three first generation biogenic acids (cis-pinic acid, pinonic acid and terpenylic acid), two second generation biogenic acids (MBTCA and diaterpenylic acid acetate (DTAA)) and three anthropogenic acids (adipic acid, benzoic acid and phthalic acid). In addition, six organosulfates were identified, of which four are hypothesized to originate from isoprene and four from monoterpenes (Surratt et al., 2008), two of which were identified as nitrooxy organosulfates.

In general, the levels of the identified carboxylic acids are comparable to results of other studies in northern Europe during spring and summer (Kristensen and Glasius, 2011; Zhang et al., 2010; Kourtchev et al., 2008; Warnke et al., 2006). Concentrations of monoterpenes and isoprene organosulfates are higher at the four sites compared to previous measurements performed in Silkeborg, Denmark, during spring 2008 (Kristensen and Glasius, 2011).

CONCLUSIONS

Figure 1. Location of the four Nordic sites participating in the SONORA sampling campaign (Yttri et al., 2011).

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Figure 2. Concentration (ng μgOC⁻¹) of 1st and 2nd generation biogenic acids, anthropogenic acids and isoprene and monoterpene derived organosulfates and nitrooxy-organosulfates in SOA collected in Bikenes, Norway (●), Hyytiälä, Finland (♦), Lille Valby, Denmark (■) and Vavihill, Sweden (▲) during August 5th to September 9th 2009.

The distribution, concentration and temporal variations of all organic acids and organosulfates are almost identical for aerosols collected at Lille Valby and Vavihill (Figure 2 and 3), most likely due to the relatively short distance (< 70 km) between the two sites. Of all acids and organosulfates, second generation biogenic acids along with anthropogenic acids constitute the largest fraction at Lille Valby and Vavihill. Interestingly, although almost 1000 km apart aerosols collected from the two rural-background stations at Birkenes and Hyytiälä show a similar composition of organic acids and organosulfates. In respect to second-generation biogenic acids, isoprene and monoterpene derived organosulfates, all four sample sites show similar temporal variations during the sampling period. In contrast, first generation acids show large differences in both concentration and temporal variation in aerosols collected at Hyytiälä and Birkenes compared to aerosols collected at Lille Valby and Vavihill. This indicates that the formation
of first generation acids may be dominated by more local sources compared to aged SOA, such as second generation acids and organosulfates. Based on the similar temporal variations at the four sites, second generation acids and organosulfates appears to be more affected by regional sources, such as long-range transportation. The higher concentration of first generation biogenic acids in SOA from Birkenes and Hyytiälä is explained by larger emission sources from the surrounding vegetation dominated by coniferous and deciduous trees.

![Pie charts showing distribution of organic acids and organosulfates in SOA collected at four sites.](image)

**Figure 3.** Distribution (%) and concentration (ng m\(^{-3}\)) of organic acids and organosulfates (OS) in SOA collected in Bikenes, Norway, Hyytiälä, Finland, Lille Valby, Denmark, and Vavihill, Sweden during August 12\(^{th}\) to September 9\(^{th}\) 2009.

Although the Nordic boreal forests are dominated mostly by monoterpene emitters, isoprene organosulfates are identified at concentrations similar to or higher than most monoterpene first-generation oxidation products (Figure 2). Furthermore, for all investigated sites, isoprene organosulfates contributes to a larger fraction of the sampled SOA compared to monoterpene organosulfates (Figure 3). This shows that isoprene may contribute an important fraction to SOA in Nordic areas.

Despite the remote and rural location of the four sampling sites, all sites show relatively high concentrations of anthropogenic acids (Figure 2). This, in combination with the similar SOA composition and temporal variations, underline the regional influence on the formation of SOA during the sampling period.

**ACKNOWLEDGEMENTS**

This work was supported by Nordic Council of Ministers, the Climate and Air Quality Group, the EU 6th framework EUCAARI (Contract 036833-2), the VILLUM FOUNDATION and UNECE (the EMEP project).
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Climate Engineering or ‘geo-engineering’ is an emerging research field, stimulated by growing concern that the ‘2-degree target’ may be becoming almost unreachable by mitigation alone. Failing to meet the target would imply a greater risk of passing tipping points in the climate system, e.g. associated with massive releases of methane from Siberian permafrost. Several climate engineering mechanisms have been proposed, and we will mainly address those that are associated with deliberate injections of particles into the atmosphere. We will show selected results from simulations using the Norwegian Earth System Model (NorESM) alone, as well as multi-ESM simulations in the context of the Geoengineering Model Intercomparison Project (GeoMIP). The main focus will be on cryospheric changes in the following three cases: 1) Future without climate engineering; 2) Future with climate engineering; 3) Future after shut-off of climate engineering, e.g., due to undesired side effects or technical failure. We will also briefly describe planned studies related to this issue in an upcoming project (EXPECT) on climate engineering, funded by the Norwegian Research Council.
LONG-TERM AEROSOL AND TRACE GAS MEASUREMENTS IN EASTERN LAPLAND, FINLAND: THE IMPACT OF KOLA AIR POLLUTION TO NEW PARTICLE FORMATION AND POTENTIAL CCN

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Keywords: new particle formation, long-term measurements, air pollution.

INTRODUCTION

Sulphur and primary emissions are decreasing largely all over Europe, resulting in increased air quality and decreased direct radiation forcing by aerosols. Changes in indirect radiative forcing however, are not well known since the decrease in CCN (cloud condensing nuclei) due to the decrease in primary production can be at least to certain extent compensated by secondary CCN production (Hamed et al., 2010; Makkonen et al., 2012) as well as climate warming (Makkonen et al., 2012; Paasonen et al., 2013).

The smelter industry in Kola Peninsula is the most important source of anthropogenic SO₂ within the Arctic domain. During the past couple of decades the sulphur emissions have been decreasing, even though they still exceed the emissions of entire Finland (Paatero et al., 2008; Prank, 2010). SMEAR I station (Station for Measuring Ecosystem-Atmosphere Relations) (Hari et al., 1994), located only 6 km from the Russian border, was established in 1991 in order to measure the impact of Kola Peninsula sulphur dioxide emissions to the forests in Eastern Lapland. In general, the station is a clean background station but during airmass transport over Kola, the sulphur dioxide concentration increases drastically (Ruuskanen et al., 2003). The highest values of SO₂ are observed in late winter and early spring (Ruuskanen et al., 2003).

New particle formation (NPF) is closely linked with SO₂ since in the atmosphere it is oxidised into H₂SO₄ which in turn is known to be the key chemical component in NPF (Sipilä et al., 2010; Kerminen et al., 2012). Via this pathway SO₂ has an effect on the condensation sink (CS), which is determined by the amount of pre-existing particles. Low CS favours NPF but on the other hand low H₂SO₄ disfavours NPF. We will investigate which of these counteracting effects is more important in Eastern Lapland and what kind of trends there are seen in SO₂ as well as aerosol and NPF related properties. We will later connect the Kola emissions to the NPF observed at SMEAR I. In the analyses, we used data from 1998 – 2011, since particle size distributions were available from 1998 onwards.
METHODS

SMEAR I station is located on top of Kotovaara hill, 390 m.a.s.l. and surrounded by 60 years old Scots pine (Pinus sylvestris) forest. The infrastructure includes a small hut for the aerosol- and trace gas analysers and a 16m high mast with instruments for meteorological, irradiance and eddy-covariance measurements. Also, some instruments have housings outside the hut and continuous chamber measurements from the Scots pines are conducted. We will use measurements of aerosol size distributions, SO$_2$ concentration as well as meteorological variables to investigate the long-term trends and the effect of Kola Peninsula smelter industry to NPF. Aerosol size distributions are measured with a Differential Mobility Particle Sizer (DMPS) (Aalto et al., 2001) and SO$_2$ is measured with a pulsed fluorescence analyser.

The days were classified into event, non-event and undefined days by visual inspection of the daily aerosol size distributions. An day was classified into event day when there was a new, growing mode appearing below 25nm (Dal Maso et al., 2005; Kulmala et al., 2012). The event days were further classified into Class I and Class II so that from Class I it is possible to calculate both growth and formation rate (GR and J$_8$ or J$_3$, respectively) whereas for Class II event this is not possible due to strong fluctuations in the mode concentration or diameter. During an undefined day, a new sub-25nm mode is appearing but the mode doesn’t grow. Particle formation rate was calculated by taking into account the time evolution of 3−25−nm (8−25−nm) sized particles and coagulation and the particle growth rate was obtained by following the nucleation mode mean diameter. We also calculated sulphuric acid proxy using two existing parameterizations: a simple linear function including only measurements of SO$_2$, CS and Global radiation (Petaja et al., 2009) as well as a non-linear parameterization including also RH, temperature and pressure (Mikkonen et al., 2011).

RESULTS AND CONCLUSIONS

On average there are 54 new particle formation days in a year, out of which from 20 Class I events. The events peak in spring with another minor peak in the autumn. However, the Class I events have been decreasing dramatically (Table 1) from about 40 to less than 10 Class I events in a year. Although the mean value of Class I events per year is clearly higher than in Western Lapland, Pallas (Asmi et al., 2011), the recent years the NPF events have levelled to the same values as in Pallas (Asmi et al., 2011). The number of events has been decreasing especially during spring and autumn in such a way that the autumn peak has disappeared. At the same time, the number of undefined days has increased during spring and the non-event days during summer and autumn.

The linear trends [%/year] of various measured and calculated parameters are shown in Table 1. The greatest decreases are obtained in SO$_2$, Condensation sink (CS), Sulphuric acid proxy and Event class I days. All particle concentrations have been decreasing except for nucleation mode concentration. Also, the formation rate of 3−nm particles has been increasing but on the other hand the apparent formation rate of 8−nm particles has been decreasing at the same time. These results suggest that cleaning of the air from industrial SO$_2$ and primary emissions has decreased the CS leading to higher J$_3$ and thus higher nucleation mode concentration but this is not reflected to the CCN-sized (cloud condensing nuclei) particles due to decreases in the primary production and on the other hand less condensable vapours (namely H$_2$SO$_4$) that could form new particles. This is especially true in spring when forest is still covered by snow and the organic emissions from the trees are very small and thus not contributing to the condensational growth as much as during summertime. It also seems that the current temperature increase is not yet sufficient enough to
compensate the loss of primary particles but it is expected that the concentrations of potential CCN would increase with increasing temperature (Paasonen et al., 2013).

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Nucleation mode concentration</td>
<td>+4.3</td>
<td>34 cm$^{-3}$</td>
</tr>
<tr>
<td>Total concentration</td>
<td>-2.5</td>
<td>549 cm$^{-3}$</td>
</tr>
<tr>
<td>Condensation sink</td>
<td>-7.7</td>
<td>9.2 · 10$^{-4}$ s$^{-1}$</td>
</tr>
<tr>
<td>$CN \geq 50$nm</td>
<td>-3.9</td>
<td>298 cm$^{-3}$</td>
</tr>
<tr>
<td>$CN \geq 80$nm</td>
<td>-4.1</td>
<td>197 cm$^{-3}$</td>
</tr>
<tr>
<td>$CN \geq 100$nm</td>
<td>-3.9</td>
<td>165 cm$^{-3}$</td>
</tr>
<tr>
<td>$CN \geq 150$nm</td>
<td>-3.2</td>
<td>103 cm$^{-3}$</td>
</tr>
<tr>
<td>$SO_2$ (1998-2011)</td>
<td>-10.9</td>
<td>0.2 ppb</td>
</tr>
<tr>
<td>$SO_2$ (1992-1997)</td>
<td>-5.7</td>
<td>0.3 ppb</td>
</tr>
<tr>
<td>$H_2SO_4$ proxy (Petäjä et al.)</td>
<td>-5.2</td>
<td>1.1 · 10$^6$molec.cm$^{-3}$</td>
</tr>
<tr>
<td>$H_2SO_4$ proxy (Mikkonen et al.)</td>
<td>-8.0</td>
<td>1.5 · 10$^6$molec.cm$^{-3}$</td>
</tr>
<tr>
<td>Event class I days</td>
<td>-9.8</td>
<td>20 /year</td>
</tr>
<tr>
<td>Non-event days</td>
<td>+3.2</td>
<td>179 /year</td>
</tr>
<tr>
<td>$J_3$ (2005-2011)</td>
<td>+23</td>
<td>0.08 cm$^{-3}$s$^{-1}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>+1.5 °C/decade</td>
<td>-0.6 °C</td>
</tr>
</tbody>
</table>

Table 1: Trends and median values of selected measured variables and calculated parameters.

Sulphur species have a big impact on both the formation and growth at SMEAR I. $H_2SO_4$ explains approximately 20 – 50% of the condensational growth and there is large seasonal variation with highest values obtained during spring (50%) and autumn (30%). These values are higher than e.g. at Pallas, in Western Lapland (Asmi et al., 2011). Using the obtained $GR$ we calculated the estimated time at which 1.5 – nm clusters were formed assuming constant growth rate below the cut-off size of DMPS. We observed that

- particles form earlier during spring due to high concentrations of $SO_2$ and $H_2SO_4$ as well as sufficient amount of radiation,
- several events have occurred during in the absence of light and they are connected to especially high concentrations of $SO_2$ and,
- high $SO_2$ concentrations can advance the onset of nucleation by several hours, especially in the presence of high global radiation.

Finally, we calculated the fraction of time that trajectories arrive over Kola in general and during event days only. The relative difference between these two was greatest during spring and autumn: during these times airmasses pass over Kola more frequently during NPF days than in general.

All in all, these results show that the sulphur emissions from Kola peninsula smelters have a large impact on the NPF observed in Eastern Lapland. It seems, however, that the NPF frequency has now levelled near the natural background level when the extra sulphur boost from Kola has decreased distinctively.

ACKNOWLEDGEMENTS

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INTRODUCTION

The increasing human activities are changing the environment and we are pushing the safe boundaries of the globe (Rökvström et al. 2009). Actions are needed to ensure that the society remains within the sustainable utilization of the resources (Leach et al. 2012). It is of utmost importance to gauge with a comprehensive research program the current status of the environment, particularly in the most sensitive locations. Pan-Eurasian Experiment (PEEX) is a multidisciplinary research approach aiming at resolving the major uncertainties in the Earth system science and global sustainability questions in the Arctic and boreal Pan-Eurasian regions. The vision of PEEX is to solve interlinked global challenges influencing the human wellbeing and societies in northern Eurasia: climate change, air quality, biodiversity loss, chemicalisation, food supply, energy production and fresh water in an integrative way, recognizing the significant role of boreal regions and the Arctic in the context of global change. The PEEX vision includes the establishment and maintenance of long-term, coherent and coordinated research activities and research & educational infrastructures in the PEEX domain. PEEX aims to contribute to the Earth system science agenda and climate policy in topics important to Pan-Eurasian environment and to provide adaptation and mitigation strategies for northern Pan-Eurasian societies to cope with climate change.

PEEX agenda is built on a bottom-up initiative by several European, Russian and Chinese research organizations and institutes. The promoter institutes here have been University of Helsinki, Finnish Meteorological Institute in Finland and Institute of Geography, Moscow State University, Aerocosmos and Institute of Atmospheric Optics Siberian Branch, RAS, in Russia. The first PEEX meeting was held in Helsinki in October 2012, followed by the second PEEX meeting in Moscow in February 2013. PEEX is based on the collaboration of Russian, Chinese and European parties and currently involves ca 40 research institutes. From European perspective PEEX experiment can be considered as a crucial part of the strategic aims of several European and national roadmaps for climate change research and the development of next generation research infrastructures.

The PEEX domain covers natural and urban environments of Northern Pan-Eurasian region. The natural environments include boreal coniferous and deciduous forests, steppe, wetlands and aquatic...
ecosystems including marshes, large river systems and freshwater bodies as well as the marine ecosystems, mountains and sub-arctic tundra ecosystems. Siberia and the Arctic Ocean is the core geographical region of the PEEX domain. The majority of the PEEX geographical domain is situation in the territory of Russia and China.

METHODS

The PEEX agenda is divided into four focus areas: F-1 Research Agenda, F-2 Infrastructures, F-3 Society Dimension and F-4 Knowledge Transfer. F-1 Research Agenda will use an integrated observational and modelling framework to identify different forcing and feedback mechanisms in the northern parts of the Earth system, and therefore enable more reliable predictions of future regional and global climate. The PEEX will apply the integrated research approach for solving the following large scale research questions.

1. How are the main climate parameters (temperature, precipitation, snow cover, cloudiness) changing in the Pan-Eurasian region over the next decades?
2. What are the important feedbacks in the Pan-Eurasian climate system and how they are related human activities and ecosystem behaviour in short (decades) and long (millennia) time scales?
3. How will the cryosphere, including the Arctic sea ice extend, snow cover and permafrost, change with changing climate?
4. How fast will the permafrost thaw proceed and how will it affect ecosystem processes and ecosystem-atmosphere feedbacks, including the hydrology and greenhouse gas fluxes?
5. How could the regions and processes especially sensitive to climate change be identified, and what are the best methods to analyse their responses?
6. Will there be tipping points in the future evolution of the Pan-Eurasian ecosystems and demographic development?
7. What are the present stage and expected changes of environmental pollution (air, water, soil) and related stresses on population and ecosystems in Eurasia, and how will these changes affect societies (livelihoods, agriculture, forestry, industry)
8. How will human actions influence further environmental change in the region?
9. How do the fast climatic changes affect the physical, chemical and biological state of the different ecosystems, inland water, coastal areas, and the economies and societies in the region?
10. How could one identify the environmental and socioeconomic areas most vulnerable to climate change, and how could their adaptive capacities be improved?

The strategic focus of the F-2 Infrastructures is to ensure the long-term continuation of advanced measurements in the land-atmosphere-ocean continuum in northern Eurasian area. Thus, one of the first steps of implementation plan is to start building the long-term, continuous and comprehensive research infrastructures (RI) in the northern Pan-Eurasia (see Kulmala et al. 2011). These RIs will include ground-based, aircraft and satellite observations as well as multi-scale modelling. The F-3 Society Dimension, is aimed to provide fast-track assessments of global environmental change issues for climate policy-making and mitigation and adaptation strategies for the northern Pan-Eurasian region.

F-4 Knowledge transfer will provide education programmes for the next generation scientists, instrument specialists and data engineers. It will distribute information for general public to build the awareness of climate change and human impact on different scales of the climate problematic and increase visibility of the PEEX activities in Europe, Russian and China. Part of the F-4 PEEX will engage the larger international scientific communities also by collaborating with, utilizing, and advancing major observation infrastructures such as the SMEAR, ICOS, ACTRIS, and ANAEE networks in addition to building its own in the Pan-Eurasian region. PEEX will promote standard methods and best practices in creating long-term, comprehensive, multidisciplinary observation data sets and coordinate model and data comparisons and development; PEEX will also strengthen the international scientific community via an extensive capacity building programme.
The implementation of PEEX agenda is based on two components: (i) coordination of existing activities and (ii) new PEEX activities. PEEX funding will be built on national, bilateral and Nordic and European funding instruments based on the matching funds concept. Furthermore, PEEX initiative will co-operate with several EC and ESA funded activities aimed to develop next generation research infrastructures and data products such as EU-FP7-ACTRIS-I3-project (Aerosols, Clouds, and Trace gases Research InfraStructure Network-project 2011-2015), ICOS a research infrastructure to decipher the greenhouse gas balance of Europe and adjacent regions and EU-FP-7 e-infra ENVRI “Common Operations of Environmental Research Infrastructures” project. PEEX will be part of the iLEAPS programme (Integrated Land Ecosystem – Atmosphere Processes Study) bringing the PEEX under umbrella of the International Geosphere-Biosphere Programme (IGBP) / Future Earth.

FUTURE PROSPECTS

PEEX will integrate a new Earth system research community in the Pan-Eurasian region by opening its research and modeling infrastructure and inviting international partners and organizations to share in its development and use. PEEX initiative will be a major factor integrating the socioeconomic and natural science communities to working together towards solving the major challenges influencing the wellbeing of humans, societies, and ecosystems in the PEEX region. PEEX research community is currently finalizing the Science Plan. The first version of the Implementation Plan will be drafted in the autumn 2013. The next PEEX-3 meeting will take place in Hyytiälä, Finland in August, 2013. PEEX aims to be operational starting from 2014.

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MODELLING THE LAKE ICE SEASON

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Keywords: lake ice, model, climatology, ice growth, deterioration

ABSTRACT

Lakes in the boreal and tundra zones possess a seasonal ice cover. Ice seasons are described by the dates of freezing and ice breakup for the ice phenology, and ice coverage and ice thicknesses for the severity of ice seasons. The freezing date is related to fall air temperature with correlation time scale depending on the lake depth. Ice growth depends primarily on air temperature and snow accumulation. Ice breakup depends on the maximum ice and snow thicknesses, solar radiation transfer, and air temperature; the onset of melting is the primary question. Lake ice models have the heat conduction law in their core, and heat is transferred through the boundaries in the ice sheet. Analytical or semi-analytical models are used for scaling question, while numerical models with congelation ice, snow-ice and snow layers serve for detailed process studies. Recently research has been made to model the deterioration of the ice sheet properly with internal melting, ice breakage and drifting. Warmer climate brings also qualitative changes to lake ice seasons by moving boundaries of ice climate zones.
INTRODUCTION

Several components of the Earth System will respond to a climate change. These climate feedbacks can either counteract (negative feedback) or facilitate (positive feedback) the original perturbation. Change in lapse rate is an example of a negative feedback: in a warmer climate the vertical temperature gradient will likely be less steep, resulting in relatively more emitted longwave radiation from Earth’s atmosphere. Cryosphere provides the Earth System with a positive feedback: increasing global temperatures act to decrease the amount of sea-ice, which leads to decreased albedo and more absorption of solar radiation.

There are also several feedbacks connected to emissions and processing of atmospheric aerosols (Carslaw et al., 2010). Climate change can modify emissions from e.g. deserts, wildfires, biosphere and oceans. Perhaps the most famous aerosol-related climate feedback is the CLAW hypothesis, which connects rising ocean temperatures to increased phytoplankton growth, DMS emissions and aerosol formation, eventually forming a negative feedback cycle (Charlson et al., 1987). A similar negative feedback can be found from continental biosphere, where increasing temperatures and photosynthesis could increase the emission of biogenic volatile organic compounds (BVOCs) resulting in an increase of aerosol mass and number (Kulmala et al., 2004). To study these biosphere-atmosphere interactions with Earth System Models, the models need to be equipped with detailed microphysical models describing secondary aerosol formation.

In this study, we improve the Norwegian Earth System Model NorESM (Iversen et al., 2013; Bentsen et al., 2013) in terms of nucleation, particle growth and secondary organic aerosol (SOA) formation. The developed model is used to study the climate effects of secondary aerosol formation in different climate and emission environments.

NUCLEATION IN NORESM

The aerosol model in NorESM1-M (Kirkevåg et al., 2013) does not include a mechanism for atmospheric nucleation, but instead, all excess sulfuric acid after condensation is assumed to form new particles of 23.8 nm in diameter. In this work, we have removed this assumption from the NorESM and introduced several nucleation mechanisms to the model. The implemented parameterizations include binary homogeneous nucleation (BHN) by sulfuric acid and water, activation-type nucleation, kinetic-type nucleation and nucleation by organic vapors. NorESM does not include ammonia, hence ternary sulfuric acid-ammonia-water nucleation is not available at the moment.

BHN is implemented throughout the atmosphere (Vehkamäki et al., 2002). The parameterization produces a high number of particles in the upper troposphere and lower stratosphere (UTLS) but
very low nucleation rates in the boundary layer. Since BHN has been shown to be inadequate for reproducing observed nucleation rates and particle concentrations in the boundary layer, we have complemented the NorESM nucleation module with several optional boundary layer nucleation mechanisms. Activation-type nucleation (Kulmala et al., 2006) assumes that the formation of new particles is linearly proportional to sulfuric acid gas concentration, \( J_{2nm} = A[H_2SO_4] \). The activation-type nucleation coefficient \( A \) should take into account factors other than sulfuric acid concentration. Naturally, these factors are not constant in time or space. Sulfuric acid concentration measurements are not abundant, and detailed information from nucleation is only available from campaigns. Paasonen et al. (2010) studied formation rates of 2 nm particles in four sites in Europe and found median \( A \) coefficient ranging from \( 6.0 \cdot 10^{-7} \) to \( 19 \cdot 10^{-7} \text{s}^{-1} \). We have applied the median value of \( 1.7 \cdot 10^{-6} \text{s}^{-1} \) (Paasonen et al., 2010) as a global activation coefficient in NorESM.

Although sulfuric acid is likely to be the main driver for atmospheric nucleation (Sipilä et al., 2010), amines, ammonia low-volatile organic vapors could play a role in the early steps of new particle formation. To account for the effect of organics on nucleation rate, we have included a parameterization which combines sulfuric acid and organics, \( J_2 = A_{S1}[H_2SO_4] + A_{S2}[ORG] \) (Paasonen et al., 2010). In this parameterization the coefficient \( A_{S1} \) is smaller than the coefficient \( A \) in pure sulfuric acid nucleation, and the nucleation rate is affected by the availability of low-volatility organic vapors. In the simulations, organic nucleation is expected to increase the natural background number concentration and decrease the anthropogenic influence, compared to activation-type nucleation.

### SOA FORMATION AND PARTICLE GROWTH

Nucleated particles of 1-2 nm size are rather irrelevant for climate as such. Further growth is needed in order to affect e.g. cloud properties. Even if the initial nucleated particle would consist mainly of sulfuric acid, organic vapors play an important role for the subsequent growth (Riipinen et al., 2011). In recent CLOUD experiments in CERN, the organic volume fraction was shown to increase from 0.4 to 0.9 when particles grew from 2 to 63 nm (Keskinen et al., 2013).

In order to improve the simulated effect of SOA formation on aerosol number, we have further developed the SOA model in NorESM. Original NorESM1-M (Kirkevä et al., 2013) introduces SOA as a "primary" emission of OC from monthly average precursor fields. The SOA is assumed to have a diameter similar to other OC emissions. We have introduced two precursor tracers for monoterpene and isoprene. The emissions of these BVOCs are taken either from monthly prescribed MEGAN2 (Guenther et al., 2006) emissions or the interactive vegetation model CLM, which is implemented in NorESM. At the moment, only monoterpene is assumed to form SOA with a 15 % yield. Compared to the original mechanism, SOA formation in the modified version can occur also above the surface level of the model.

In NorESM, we have taken into account the growth by both sulfuric acid and organics in the size range 1-24 nm. The formation of nucleation mode particles \( (J_x) \) is estimated from the nucleation rate \( J_{nuc} \) as (Lehtinen et al., 2007)

\[
J_x = J_{nuc} \exp \left( -\gamma \cdot d_{nuc} \frac{CoagS(d_{nuc})}{GR} \right),
\]

where the coagulation sink \( CoagS \) is calculated from the NorESM particle population and particle growth rate \( GR \) from sulfuric acid and low-volatility organic vapor concentration. We assume that 50 % of the monoterpene ozonolysis products are enough low-volatile that they can partition to the nucleated particles (below 24 nm). Currently, the information of SOA mass from new particle formation is lost, since OC mass is not transported in the nucleated mode. Improving the microphysical module to take into account SOA mass fraction is under work.
ROLE OF NUCLEATION IN SIMULATED PARTICLE CONCENTRATIONS

Fig. 1 shows the observed and simulated aerosol number concentrations at Arctic stations Värriö and Zeppelin, and high altitude sites Moussala and South Pole. The simulated results are shown from experiments with and without nucleation. In Värriö, simulations without nucleation are clearly unable to reproduce observed concentrations outside winter months. Including nucleation in the model improves the simulated seasonal cycle, although summer concentrations are overestimated. Using organic nucleation increases summer maximum even further. The observed concentrations at Zeppelin station are almost a magnitude lower than those in Värriö, and the station is less influenced by continental biogenic emissions. All simulations capture the concentration variability rather well, although with some overestimation during October-January. In the high altitude site Moussala the observed concentrations are well reproduced by the model with nucleation included, however, the results are rather insensitive to the selected nucleation rate parameterization (activation-type or organic nucleation). The extremely low winter concentrations in South Pole are somewhat overestimated, but the overall intra-annual variation is well captured. Nucleation has very little effect in the Antarctic aerosol number concentrations, which are simulated extremely well by all experiments.

![Figure 1: Simulated and observed total aerosol number concentrations (cm$^{-3}$) in Värriö, Zeppelin, Moussala and South Pole. Three simulations are shown: without any nucleation (blue dashed line), activation-type nucleation (blue) and nucleation including organic vapors (green). The pie charts represent the fractional contribution of aerosol components to number concentration: SS=sea salt, SO4=sulfate, OM=organic matter, DST=dust, BC=black carbon.](image)

In Makkonen et al. (2013), the aerosol number concentrations of NorESM are evaluated against 60 stations and 12 vertical profiles from flight observations. Altogether 10 sensitivity experiments are used to study the effects of SOA formation, black carbon size distribution and nucleation on aerosol number concentration. Including nucleation in the simulations improves the simulated concentrations in terms of aerosol number bias and seasonal cycle (Makkonen et al., 2013).
EFFECT OF NUCLEATION ON CLOUD PROPERTIES

While nucleation plays an important role for the total number concentration of aerosols, the effect on larger particles is dampened by particle losses during growth from nanometer size to e.g. CCN sizes. Fig. 2 shows the simulated increase in cloud droplet number concentration (CDNC) due to nucleation in June. It should be noted that in the reference simulation without nucleation, the sulfuric acid can still condense on existing particles, providing also growth towards CCN sizes. With less competition on condensing vapors in the case of no nucleation, certain particles might reach CCN size more easily. Generally over Northern Hemispheric continents, nucleation increases CDNC by more than 10%. In North America and central Eurasia, the effect can exceed even 50%. The CDNC increment due to nucleation is highest during summer months, partly due to photochemistry and availability of biogenic organic vapors.

Figure 2: Change in simulated cloud droplet number concentration (at 970 hPa level) due to nucleation in June.

ENVIRONMENTAL CHANGES MODIFYING NEW PARTICLE FORMATION

As nucleation is sensitive to sulfuric acid concentration, it is affected by both natural (e.g. DMS, volcanoes, wildfires) and anthropogenic sources (SO$_2$ from e.g. industry, traffic). The climate effect of nucleation is highly dependent on availability of particle growth, where biogenic VOC emissions could play an important role. The strength of certain natural sources could be changing as a response to climate change or anthropogenic influence. The aerosol and precursor emissions from anthropogenic sources have generally been increasing from pre-industrial to 1970-1980, when emission regulations became effective in many regions. Possible future decreases in anthropogenic emissions can induce large changes in the aerosol cooling effects (Makkonen et al., 2012).

We have used the NorESM to study both the effect of anthropogenic emissions and natural responses on new particle formation. Fig. 3a shows the evolution of simulated particle number concentration between years 1950 and 2000, when only changes in anthropogenic emissions are considered (Lamarque et al., 2010). SO$_2$ emissions and aerosol number concentration in Asia have increased rather steadily in the simulations, while number concentrations in Europe and North America have been declining since the 1980s. In the applied emission inventory the peak in SO$_2$ emission was in the 1970s in both Europe and North America, but the modeled number concentrations are also sensitive to emissions of fossil fuel BC, which peaked in the 1980s.

The NorESM provides an excellent framework to study interactions between Earth System components. Earth System feedbacks are an essential part of CRAICC. We have used the model
Figure 3: Evolution of total aerosol number concentration (cm$^{-3}$) from the year 1950 to year 2000 (a) and the response of aerosol growth rate to temperature change (b). Each point in (b) represents one simulated year.

... built in this work to study the negative BVOC-aerosol-climate feedback: increasing temperatures (and photosynthesis) would act to increase BVOC emissions, which in turn would increase aerosol concentrations and cause more aerosol cooling (Kulmala et al., 2004). We have run a set of 4 simulations: control simulations with and without interactive BVOC emission, and two climate change simulations perturbated with 2xCO$_2$ concentration. Fig. 3b shows the response of aerosol growth rate (GR in Eq.1) to the changing climate. With constant BVOC emissions (prescribed monthly emission, red dots), the growth rate changes only slightly with changing climate. However, there is a clear signal to the aerosol growth rate when BVOC emissions can respond to the climate change. The growth rate increase due to 1.5-1.8 K temperature change is $\sim$20%. The increase in aerosol mass, aerosol growth rates and survival of nucleated particles can cause a significant additional aerosol cooling to counteract the initial climate change.

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RECENT ADVANCES IN ION AND AEROSOL MEASUREMENTS


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Keywords: Atmospheric aerosol particles, long-term measurements, PBL, laboratory studies.

INTRODUCTION

Aerosol and Ion group at University of Helsinki has a comprehensive long-term experience of ground-level aerosol measurements. Measurements of ambient aerosol size distributions were started at the SMEAR II station at Hyytiälä, Finland, in January 1996, and have been on-going since then. We are especially interested in these size distribution data to characterize and parameterize periods of new particle formation and growth. Secondary formation of atmospheric aerosol particles, so-called new particle formation (NPF), is believed to be the dominant source of aerosol particles in the atmosphere. Nucleation is a process of gas-to-particle conversion, beginning with a few gas molecules colliding to form a cluster of 1-2 nm in diameter (Kulmala et al., 2013). This first step of NPF is followed by the growth of the newly formed particles. NPF is a frequent phenomenon in the lower atmosphere. Recent development in the aerosol instrumentation to measure the critical particle size below 3 nm in size has enabled the direct detection of the newly formed particles connecting the gas and particle phases (Kulmala et al., 2012).

At this moment, the mechanisms of particle formation and the vapours participating in this process are not truly understood. Especially, in which part of the atmosphere the NPF takes place, is still an open question. Until now, there exists only a few atmospheric dataset measured in lower troposphere over the Northern boreal forests. Our aim is to supplement the on-ground measurements with airborne measurements to cover the cryosphere-aerosol-cloud-climate interactions within the planetary boundary layer (PBL). The PBL is chemically and physically the most dynamic part of the atmosphere as it has high loading of aerosol particles and their gaseous precursors.

ADVANCES IN UNDERSTANDING ATMOSPHERIC FORMATION AND GROWTH IN THE LOWER ATMOSPHERE

We measured the chemical and physical processes within the PBL to detect directly the very first steps of NPF in the atmosphere. These measurements of the vertical and the horizontal extension of NPF events were performed using an instrumented airship, Zeppelin. The vertical profile measurements (altitudes up to 1 km) represent the particle and gas concentrations in the lower parts of the atmosphere: the residual layer, the nocturnal boundary layer, and the PBL. At the same time, the ground based measurements records present conditions in the surface layer. Horizontal, almost Lagrangian, experiments are possible as the airship drifts with the air mass. The main nucleation campaigns were performed in Po Valley, Northern Italy (summer 2012), and Hyytiälä, Southern Finland (spring 2013).

The key instruments on-board Zeppelin to measure the onset of NPF were Atmospheric Pressure interface Time-Of-Flight mass spectrometer (APi-TOF), a Particle Size Magnifier (PSM), and a Neutral cluster and Air Ion Spectrometer (NAIS). Instruments are described in more detailed in Kulmala et al. (2013) and reference therein. These instruments are able to measure particles at the size range ~1-2 nm where atmospheric nucleation and cluster activation takes place. The high time resolution of the instruments allowed us to observe the starting time, location and altitude of the NPF. These measurements are part of
the PEGASOS project which aims to quantify the magnitude of regional to global feedbacks between the atmospheric chemistry and physics, and thus quantify the changing climate. The Zeppelin flights are observing radicals, trace gases, and aerosols inside the lower troposphere over Europe.

We use also a small Cessna 172 one-engine aircraft with slow velocity (air velocity around 130 km/h) operating between altitudes of 300 m and 3.5 km (Schobesberger et al., 2013). The Cessna flight campaigns have been on-going since spring 2010. We measured vertical profiles up to 3.5 km above the countryside of Southern Finland which is patched with boreal forests of different ages, mires, small lakes, and cultivated land. The aircraft carries comprehensive instrumentation to measure aerosol particle and trace gas properties, and meteorological parameters. The Cessna is able to fly much higher altitudes and cover wide areas, whereas Zeppelin is able to stay over fixed location and fly very low altitudes. The Cessna can easily reach the free troposphere conditions even when the PBL is fully thermally mixed and fly close to cloud deck to study aerosol-cloud interactions, whereas Zeppelin scans the air from first 1000 meters.

ADVANCES IN INTRUMENTAL DEVELOPMENT AND LABORATORY STUDIES

In the atmosphere, the mechanisms and vapours contributing to the initial aerosol growth after the cluster formation are not completely understood, which is partly because of the lack of instruments capable of measuring atmospheric clusters and particles between 1 and 3 nm. The break-through to measure neutral particles in sub-3 nm size range was made with the PSM (Airmodus A09, Vanhanen et al. 2011) which measures particles down to the mobility diameter of about 1 nm. The PSM is a mixing-type CPC, in which the aerosol is turbulently mixed with air saturated with diethylene glycol. The 50% activation diameter of the instrument can be varied between about 1–2 nm in mobility diameter by changing the mixing ratio of the saturator and sample flows.

In addition to the PSM’s capabilities, to measure the sub-7 nm growth rates and get the first indirect measurements of the particle chemical composition between 2 and 3 nm, we built a nano Condensation Particle Counter Battery (nano-CPCB, Kangasluoma et al., 2013) which consists of four CPCs optimized for the detection of sub-3 nm particles, using diethylene glycol, water, and butanol as the CPC working fluids. The nano-CPCB was calibrated with seven different test aerosols, and the size, charge and composition dependent response was obtained for each CPC. From the ambient relevant test aerosols, ammonium sulphate and sodium chloride showed a clear preference to water activation, whereas organics showed preference to butanol activation, which is the foundation of obtaining indirect information from atmospheric aerosols. After the calibration, a TSI nano-DMA was integrated to the nano-CPCB, which was then deployed in an intensive field campaign in Hyytiälä in spring 2013.

On the other hand, laboratory experiments in the CLOUD-chamber (Kirkby et al., 2011) can be also used to study the cryosphere-aerosol-cloud interactions. In the forthcoming CLOUD8 (October-December 2013), 46 instruments from 14 institutes will be deployed around the CLOUD-chamber at CERN to study the effect of the charges on aerosol activation to ice and droplet for temperature condition varying from -65C to +20C. The aerosol will consist of a control mixture of monodisperse aerosol produced in an evaporator and flush inside the chamber. In order to create a cloud inside the chamber, the chamber wall is first covert with ice, creating a saturated relative humidity over ice of 100% inside the chamber. The activation of the cloud is then created by a precisely control adiabatic expansion. The NAIS measuring the ions and neutral cluster concentration has been rebuilt to support such pressure changes. In addition, the NAIS will operate at temperature below 0C, when needed, in a temperature control environment, reducing possible artefact due to ions evaporation. To complete the setup, a SMPS (Scanning Mobility Particle Sizer) and possibly a PSM with fast response time to allow measurement of coagulation between droplet and inactivated aerosol (interstitial).
ADVANCES IN CONNECTING ATMOSPHERIC ELECTRICITY AND AEROSOL-CLOUD INTERACTIONS

Small ions are part of the atmospheric aerosol spectrum, and in atmospheric sciences study of ion-aerosol interactions is essential. Small ions are small molecular clusters carrying a net electric charge. They are produced by ionisation of molecules in the air. Ion-induced NPF is limited by the ion production rate. The results indicate that particle formation seems to dominate over ion-mediated mechanisms, at least in the boreal forest conditions.

Atmospheric ions play an important role in the fair weather electricity. Atmosphere’s fair weather condition concerns the electric field and the electric current in the air as well as the air conductivity. On the other hand, atmospheric ions are important for Earth’s climate, due to their potential role in secondary aerosol formation. This can lead to increased number of cloud condensation nuclei (CCN), which in turn can change the cloud properties. Our aim is to quantify the connections between these two important roles of air ions based on field observations and existing data archives. We studied the interactions between atmospheric electricity (air conductivity, electric field, and ambient concentration of small ions), aerosol particles, and cloud properties. In other words, the correlations and trends in atmospheric ionization, electricity, aerosols, and CCN properties were studied.

OUTLOOK

Within our group, the recent advances have been obtained after collaborative research efforts between laboratory experiments and comprehensive field observations. Thus, the long-term field observations and detailed laboratory and field campaigns are both needed in the future to characterize the cryosphere-aerosol-cloud-climate interactions. The air quality and climate interactions are not neglected. And our measurements are part of international measurement networks e.g. SMEAR, WMO-GAW, NOAA and ACTRIS.

ACKNOWLEDGEMENTS

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SNOW REFLECTANCE AFFECTED BY SOOT, VOLCANIC SAND, AND GLACIOGENIC SILT DEPOSITED ON SNOW

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Keywords: SNOW, REFLECTANCE, ARCTIC, BLACK CARBON, VOLCANIC.

INTRODUCTION

Snow surface reflectance and albedo depend on snow properties as well as environmental conditions; e.g. on impurities deposited on the snow (e.g., Wiscombe and Warren, 1980; Warren and Wiscombe, 1980). Within the NCoE CRAICC (Cryosphere-Atmosphere Interactions in a changing Arctic Climate, http://www.atm.helsinki.fi/craicc/), our snow reflectance and albedo activities include: a) long-term UV albedo measurements on Arctic seasonal snow at Sodankylä, North-Finland, combined with weekly analysis of EC/OC in snow; b) experimental field campaign measurements on snow albedo and reflectance changes at 320-2500 nm, induced by artificial deposition of soot, volcanic sand and glaciogenic silt, within the SoS-2013 experimental field campaign in Sodankylä.

LONG-TERM ARCTIC MEASUREMENTS ON UV ALBEDO

Since 2007, the local UV albedo of snow at the Sodankylä Arctic Research Centre (67°22’N, 26°39’E, 179 m asl), Finland, is measured at the operational albedo field. UV albedo measurements were planned and initiated as part of the International Polar Year IPY-2007 activities (IPY project ORACLE-O3) (Meinander et al., 2008). Two sensors of UV Biometer Model 501 from Solar Light Co. (SL501) with similar spectral and cosine responses are used, one facing upwards and one downwards, at a height of 2 m. The SL501 spectral response resembles the action spectrum for erythema, wavelengths in the UVB (280–310 nm) are most weighted. The albedo of snow (A) is the ratio of the up-welling UV irradiance to the down-welling irradiance (A = UVery↑/UVery↓), at 2π angle.
EC/OC IN SNOW IN SODANKYLÄ

Since 2009, weekly analysis of EC/OC in snow have been made during snow time at one place in the Sodankylä Arctic Research Center. The snow sample is melted, and the melt water is filtered through micro-quartz filters. A hand pump is attached to the filtering system to create a vacuum during filtering. The volume of melt water is noted and used for concentration conversions. Dried filters are thereafter analyzed in a Thermal/Optical Carbon Aerosol Analyzer (OCEC) (Sunset Laboratory Inc., Forest Grove, USA) for their apparent EC concentrations at the University of Stockholm, Sweden (J. Ström and P. Tunved).

THE SOS-2013 EXPERIMENT

The Soot on the Snow (SoS-2013) experiment was carried out in Sodankylä to study the effects of deposition of Black Carbon (BC), Icelandic volcanic sand and glaciogenic silt on the surface albedo and melt of seasonal snow. The BC was soot originating from chimneys above residential wood-burning fireplaces in Helsinki, except one spot with soot from a chimney of an oil burner, and one with soot from peat-burning power plant. The volcanic sand was near black mixture of the volcanic ash of glaciofluvial nature, originating from under the Myrdalsjokull glacier, which may be mixed with the ash of the Eyjafjallajokull eruption in 2010 and the Grimsvotn eruption in 2011. The glaciogenic silt was lighter in colour, from light-brown to slightly yellowish, consisting mainly of silt and some coarse clay sized particles, capable of being transported and deposited on the local glaciers as well as several hundreds of kilometres towards the Europe.

Thirteen spots of different concentrations of soot, volcanic sand, and silt were generated by blowing the impurities on natural snow. We also had an untouched reference measurement spot. The impurities were deposited only once to each spot, and thereafter the spots were monitored until the snow was melted. The sites were left to develop naturally, introducing as little disturbance as possible. Continuous broadband albedo was measured using pyranometers installed on seven spots. Snow samples were collected for their elemental carbon (EC) and organic (OC) concentration analysis with the Thermal/Optical Carbon Aerosol Analyzer (OC/EC), following the NIOSH 5040 protocol.

The spectral reflectance of the melting snow was measured using two ASD spectrometers, one measuring in the UV-B spectral range (325-1075 nm), and the other from UV-A up to IR (350-2500 nm). Using an ASD spectrometer coupled with the contact probe, the spectral reflectance of the volcanic sand and glaciogenic silt were determined under laboratory conditions. (Fig.1)

Figure 1. The snow reflectance and albedo activities in Sodankylä within CRAICC: a) long-term UV albedo measurements on the operational albedo field. b) Sodankylä weekly analysis of EC/OC in snow. c) The SoS-2013 experiment in Sodankylä: artificial deposition of soot, volcanic sand and glaciogenic silt.
CONCLUSIONS

Using continuous Sodankylä UV albedo data, we can study Arctic snow UV albedo over a time scale ranging from the momentary 1-min values, up to 6 years of data (2007-2013). A more detailed study of the Sodankylä UV albedo measurements has been published in Meinander et al. (2008). We have found the albedo of spring time melting snow to decrease during one day, asymmetrically to SZA. Thus, during one day, the snow albedo is in the morning ~10 % higher than in the afternoon.

The Sodankylä EC/OC in snow results allow us to study the variability of carbon in snow during winter and spring time. We have recently reported (Meinander et al. 2013) that the high concentrations of carbon in snow in Sodankylä, detected by the thermal–optical method, were in 2009-2011 data (Table 1) due to air masses originating from the Kola Peninsula, Russia, where mining and refining industries are located. For snow albedo, these amounts of carbon may produce albedo values as low as 0.5-0.7 (Fig.2).

Table 1. EC [ppb] in the spring season (1 January till snow melt) snow samples of the Sodankylä Arctic Research Center in 2009-2011. (Table modified from Table 3 of Meinander et al. (2013)).

<table>
<thead>
<tr>
<th>Date in 2009</th>
<th>EC [ppb]</th>
<th>Date in 2010</th>
<th>EC [ppb]</th>
<th>Date in 2011</th>
<th>EC [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2.2009</td>
<td>23.6</td>
<td>22.1.2010</td>
<td>84.2</td>
<td>28.1.2011</td>
<td>15.8</td>
</tr>
<tr>
<td>27.2.2009</td>
<td>19.1</td>
<td>29.1.2010</td>
<td>54.7</td>
<td>4.2.2011</td>
<td>10.3</td>
</tr>
<tr>
<td>6.3.2009</td>
<td>22.7</td>
<td>5.2.2010</td>
<td>16.8</td>
<td>11.2.2011</td>
<td>19.0</td>
</tr>
<tr>
<td>13.3.2009</td>
<td>20.6</td>
<td>12.2.2010</td>
<td>16.1</td>
<td>18.2.2011</td>
<td>37.6</td>
</tr>
<tr>
<td>13.3.2009</td>
<td>38.5</td>
<td>19.2.2010</td>
<td>15.7</td>
<td>25.2.2011</td>
<td>73.8</td>
</tr>
<tr>
<td>27.3.2009</td>
<td>41.5</td>
<td>5.3.2010</td>
<td>32.6</td>
<td>11.3.2011</td>
<td>25.2</td>
</tr>
<tr>
<td>10.4.2009</td>
<td>106.3</td>
<td>19.3.2010</td>
<td>24.1</td>
<td>25.3.2011</td>
<td>13.1</td>
</tr>
<tr>
<td>17.4.2009</td>
<td>15.7</td>
<td>26.3.2010</td>
<td>9.4</td>
<td>2.4.2011</td>
<td>23.6</td>
</tr>
<tr>
<td>24.4.2009</td>
<td>87.1</td>
<td>2.4.2010</td>
<td>23.2</td>
<td>8.4.2011</td>
<td>60.2</td>
</tr>
<tr>
<td>30.4.2009</td>
<td>85.7</td>
<td>9.4.2010</td>
<td>32.3</td>
<td>15.4.2011</td>
<td>79.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.4.2010</td>
<td>26.7</td>
<td>22.4.2011</td>
<td>90.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.4.2010</td>
<td>59.3</td>
<td>29.4.2011</td>
<td>51.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30.4.2010</td>
<td>52.9</td>
<td>6.5.2011</td>
<td>42.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.5.2010</td>
<td>56.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.5.2010</td>
<td>59.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. The SNICAR simulated snow albedo spectra at 0.3 – 1.3 µm; clear sky, SZA = 55 deg, grain radius 1.5 mm, snow depth 10 cm, snow density 350 kg/m$^3$; for clean snow (blue, 0 ppb), realistic snow (green, 200 ppb, and with MAC=10, purple), demonstrating that the absorption caused by impurities in snow is the bigger the shorter the wavelength. (Figure modified from Fig. 10 of Meinander et al. (2013)).
During the series of Soot on Snow campaigns (SoS) designed by Aki Virkkula in 2011, 2012 and 2013, we have gained information on the effects of soot on snow reflectance and albedo. The first campaign in 2011 was most of all to test the methods. In the SoS-2012 experiment, the NILU-UV multiband radiometer results showed (Table 2) that if the albedo values for the clean snow (reference spot, EC = 87 ppb) were $A_{\text{VIS}} = 0.92$ and $A_{\text{UV}} = 0.70$, then immediately after application of soot of EC = 4916 ppb in the snow, the albedo of the mid-dark soot spot was $A_{\text{VIS}} = 0.29$ and $A_{\text{UV}} = 0.28$.

Table 2. NILU-UV albedo (0-1) at UV and VIS, and elemental carbon (EC) [ppb] values of snow at SoS-2012 experiment. For the EC analysis from the reference spot, one surface sample and a vertical profile of every 5 cm were taken; for the sooted spot, three surface samples were taken.

<table>
<thead>
<tr>
<th>Albedo (0-1) / EC [ppb]</th>
<th>ASCOS-2008 87°N</th>
<th>SoS-2012 Jokioinen Reference spot Average (std)</th>
<th>SoS-2012 Jokioinen Spot1 Average (std)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>0.91-0.92</td>
<td>0.70 (0.08)</td>
<td>0.28 (0.10)</td>
</tr>
<tr>
<td>VIS</td>
<td>0.91-0.92</td>
<td>0.92 (0.03)</td>
<td>0.29 (0.01)</td>
</tr>
<tr>
<td>EC (all) / EC (top)</td>
<td>Clean Arctic Sea ice and snow at 87°N</td>
<td>160 (113)</td>
<td>4916 (1909)</td>
</tr>
<tr>
<td></td>
<td>87 (-)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the important task of separating the natural and anthropogenic effects of BC on snow albedo, we need the knowledge of the natural variability of albedo and EC of snow. Our data from Arctic Finland (Sodankylä) show that concentrations of up to 200 ppb EC (for more detailed analysis on the EC results, see Meinander et al. 2013) in natural snow, can result in UV albedo during melt time of 0.5-0.7, and 0.8 during accumulation. At the same time the snow grain size diameter $D$ varied from 0.2 mm (accumulating snow) up to several millimeters (melting snow). For a comparison: we have measured that the clean Arctic Sea ice and snow at 87°N has $A = 0.91 – 0.92$ both in the UV and VIS (Paatero et al. 2008), consistent with the small absorption coefficient of ice. Our SoS-2012 results show that in case of natural snow at southern Finland, albedo was $A=0.92$ in the VIS and $A=0.70$ in the UV. Introducing an amount of EC=4916 ppb soot on the surface of snow, decreased that albedo immediately into $A=0.28-0.29$ in both the UV and VIS.

The SoS-2013 experiment will give us more detailed information on the connection of EC and albedo of snow. The preliminary new results on volcanic sand suggest that introducing the volcanic sand with $A = 0.003$ (between 320-1075 nm) on the snow surface, causes two weeks later the albedo of melting snow to reduce down to 0.7 at the beginning of the measurement spectrum, while at the same time the albedo of the reference natural snow is close to 1 (Fig. 3). The results demonstrate that soot and volcanic sand reduce snow reflectance at UV and VIS more than glaciogenic silt, compared to natural reference snow. Yet, the apply of silt appears to result in lower VIS reflectance than the reference snow.
ACKNOWLEDGEMENTS

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REFERENCES


SOLVING GAS PHASE ATMOSPHERIC CHEMISTRY MYSTERIES IN THE BOREAL FOREST

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Keywords: MODELLING, GAS PHASE CHEMISTRY, HUMPPA-COPEC-10, VOC, OH-REACTIVITY

INTRODUCTION & METHODS

With it’s definite potential for influencing everyone’s life, global warming has drawn the World’s attention and so has boreal forest, since it is one of the areas that are expected to heat most during the future climate warming (2 – 10°C predicted by IPCC 2006).

During the summer 2010 (12 July – 12 August) one of the most extensive field measurement campaigns were conducted at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations), Hyytiälä, Southern Finland (Hari and Kulmala, 2005): HUMPPA-COPEC-10 (Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry 2010). This summer was significantly warmer than usual, which gives us a great possibility to study the future situation in a boreal forest during climate warming.

Here we present model–measurement comparison of gas phase chemistry during the HUMPPA-COPEC-10 campaign. Information about the campaign and measurements can be found in Williams et al., 2011. Our aim is to explain the atmospheric chemistry that takes place in a boreal forest ecosystem during summer and during the future climate warming. Simultaneously, we will validate our 1D vertical chemistry transport model SOSA (Model to Simulate the concentrations of Organic vapors and Sulfuric Acid) (Boy et al., 2011) which we use for the model simulations. SOSA includes modules for meteorology (SCADIS), emissions (MEGAN) (Guenther et al., 2006), and chemistry (MCM version 3.2 and KPP) (Damian et al., 2002).

RESULTS AND DISCUSSION

We divide our results into two parts: 1) dealing with the inorganic chemistry, including investigations in the OH budget, the oxidation capacity (importance of OH, O₃, and NO₃ at different times during day and night), the nitrogen cycle and measurement–model comparison of: OH, H₂SO₄, H₂O₂, NO₃, N₂O₅. 2) VOC (volatile organic compounds) chemistry, including characterisation of their fluxes, concentrations and compositions. The influence of genetic chemotypes on model simulations are evaluated. Soil emissions are normally not included into atmospheric models due to limited or no measured soil emission data, and no parametrisation of soil emissions are currently available. During the campaign soil emissions of monoterpenes and isoprene were conducted and an algorithm was prescribed and tested for these emissions. We have further investigated the effect of including organic soil emissions on the OH-reactivity, which seems to be crucial near the forest floor (< 5 m). This is very important to keep in mind, when comparing measured and modelled gas concentrations, since concentrations of atmospheric compounds are mostly conducted near ground.
ACKNOWLEDGEMENTS

The authors are very grateful for the HUMPPA-COPEC-10 team from MPI Mainz and University of Helsinki for providing data for which this study would not be possible. Furthermore, we thank the doctoral program ACCC (Atmospheric Composition and Climate Change), the Finnish Center of Excellence (FCoE), the Helsinki University Centre for Environment (HENVI) and the Cryosphere-Atmosphere Interactions in a Changing Arctic Climate (CRAICC) for financial support and the CSC – IT Center for Science Ltd for computational resources.

REFERENCES


PHYSICAL ATMOSPHERIC PARAMETERS OF ARCTIC AEROSOLS

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Keywords: Arctic aerosols, short-lived climate forcers, nucleation events

INTRODUCTION

The Arctic environment is changing rapidly and some of the reasons haven’t been qualitatively identified. While local anthropogenic emissions are few, it is known that long-range transport of air pollutants plays a major role in the dramatic climatic changes observed in the Arctic leading to the melt of sea and inland ice. In contrast to long-lived greenhouse gases, the so-called short-lived climate forcers including aerosols, black carbon, ozone and methane offer an opportunity for mitigation strategies as a reduction in these species would affect the climate directly on relatively short time scales. It is thus of great importance to quantify short-lived climate forcers in the Arctic environment and understand their transport and transformation pathways as well as their possible local emissions.

METHODS

Physical and chemical parameters were studied at “Flygers Hut” (81°36’N, 16°40’W, 30m asl) located ca. 2.5 km south-east of a military camp, Station Nord. Particle number size distributions were measured with a Scanning Mobility Particle Sizer (SMPS) in the size range from 10 to 900 nm. Atmospheric gas concentrations of ozone and NOx were measured using gas monitors (API model 400/400A and API model M200AU). Additionally, snow samples were collected in the surroundings of the station and analysed for EC/OC mass concentrations using a thermal optical carbon analyser.

Table 1. List of physical and chemical parameters, the corresponding analysis methods, time resolutions and time periods of measurements at Station Nord.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time resolution</th>
<th>Time period</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric EC/OC</td>
<td>Weekly</td>
<td>08/2008 – present</td>
<td>Thermal optical method</td>
</tr>
<tr>
<td>Atmospheric sulphate</td>
<td>Weekly</td>
<td>03/2007 – present 1995 -2002 also avail.</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>EC/OC in snow samples</td>
<td>-</td>
<td>10 samples in 04/2013</td>
<td>Thermal optical method</td>
</tr>
<tr>
<td>Atmospheric BC (Black Carbon)</td>
<td>Weekly</td>
<td>03/2008 - present</td>
<td>Particle Soot Absorption Photometer</td>
</tr>
<tr>
<td>Particle number size distribution</td>
<td>5 min.</td>
<td>07/2010 – present</td>
<td>Scanning Mobility Particle Sizer</td>
</tr>
<tr>
<td>Ozone</td>
<td>Hourly</td>
<td>03/2007 – present 1995 -2002 also avail.</td>
<td>Gas monitor</td>
</tr>
<tr>
<td>NOx</td>
<td>Hourly</td>
<td>03/2007 – present 1997 -2002 also avail.</td>
<td>Gas monitor</td>
</tr>
</tbody>
</table>

The absorption coefficient was determined using a custom built Particle Soot Absorption Photometer (PSAP) which is operated at a wavelength of 550 nm. The concentration of sulphate was monitored on weekly TSP samples collected with a filter pack sampler using ion chromatography. The EC/OC concentration was obtained using a thermal optical carbon analyser (Sunset laboratory, OR) on PM10 samples collected with a high volume sampler that was placed in the military camp. The observed
similarity of the concentration patterns of black carbon and sulphate in addition to a comparison of black carbon with model results have been reported earlier (Grube et al., 2011). The parameters measured at Station Nord are listed in Table 1.

PRELIMINARY RESULTS

Results of this work will focus on the preliminary evaluation of the particle number size distributions obtained since July 2010 at Station Nord. In general, a pronounced accumulation mode was observed during the winter and early spring months. This period coincides with the Arctic haze period as stated by other authors (Heidam et al., 2004; Nguyen et al., 2013).

As the station is very remote, local pollution caused by the service car at the station could be identified by short-lived spikes of NO\textsubscript{x}, which were observed occasionally over the years. These events were accompanied by the occurrence of small particles in the particle number size distribution, which only lasted for very short periods.

A number of nucleation events could be identified in the particle number size distributions mostly during summer. It must be noted that Station Nord is very special without any sunlight during the winter months. Freshly nucleated particles, which were not connected to local pollution events, were thus only observed during daylight periods.

The data show complex interplays between ozone, NO\textsubscript{x} and the occurrence of nucleated particles. From the current perspective, these interplays are not clearly understood and must be investigated further. The presence of ozone as an oxidant is known to favour the occurrence of nucleation events as it supports the production rate of condensable vapors that produce freshly nucleated particles (Kulmala et al., 2004). In Figure 1, nucleation events observed during June 2012 are demonstrated in a three-dimensional plot.

![Figure 1. Three-dimensional plot of particle number size distributions at Station Nord measured from June 1\textsuperscript{st} to June 30\textsuperscript{th} in 2012.](image)

ACKNOWLEDGEMENTS

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CHARACTERISATION OF HUMIC-LIKE SUBSTANCES IN ARCTIC AEROSOLS

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Keywords: HULIS, BROWN CARBON, ARCTIC, AEROSOL MASS

INTRODUCTION

Humic-like substances (HULIS) are comprised of high molecular-weight compounds which contribute substantially to organic aerosol mass. This class of compounds also relate to “brown carbon” due to their light-absorbing properties. This study presents the first investigation of HULIS in the high-Arctic atmosphere (Nguyen et al., 2013), where the presence of HULIS in the atmosphere and their possible deposition on ice and snow-covered surfaces affects the Earth’s radiative balance. The chemical characterisation and mass contribution of HULIS to organic carbon (OC), water soluble organic carbon (WSOC) and total suspended particles (TSP) were studied on twelve weekly aerosol samples collected every 4th week in 2010 at Station Nord, North East Greenland.

METHODS

The main monitoring site at Station Nord “Flygers Hut” (81°36’N, 16°40’W, 30m asl) is located 2.5 km southeast of a small Danish military station. The location was selected due to the minimal local air pollution (Heidam et al., 2004). Filter sampling collecting PM10 on quartz fibre filters was performed using the high volume sampler which was located inside the military station. Total suspended particles (TSP) were collected using a filter pack sampler (FPS) which was located inside the Flygers Hut.

HULIS was extracted from PM10 samples following a procedure adapted from Varga et al. (2001) and subsequently characterised using High Performance Liquid Chromatography- Mass Spectrometry - Mass Spectrometry (HPLC-MS-MS) regarding their selected functional groups and average molecular weight. Analysis of organic carbon (OC) content was performed on the PM10 quartz fibre filters, the water soluble organic carbon (WSOC) and the HULIS component. The PM10 quartz fibre filters were also analysed for their elemental carbon (EC) content. Suwannee River Fulvic Acid (SRFA) and Nordic Aquatic Fulvic Acid (NAFA) were included as references in both HPLC-MS-MS and carbon analysis. The total aerosol mass of TSP was also constructed following an approach by Maenhaut et al. (2011).
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analytical method</th>
<th>Period</th>
<th>Uncertainty</th>
</tr>
</thead>
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<tr>
<td><strong>TSP FPS nitro cellulose filters</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Al, S, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Se, Sr, Pb</td>
<td>Proton Induced X-ray Emission (PIXE)</td>
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<td>20%</td>
</tr>
<tr>
<td></td>
<td>Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)</td>
<td>03-12/2010</td>
<td>20%</td>
</tr>
<tr>
<td>SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, Cl$^-$</td>
<td>Ion Chromatography</td>
<td>01-12/2010</td>
<td>20%</td>
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<tr>
<td>$\text{Na}^+$</td>
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<td>01-02/2010</td>
<td>20%</td>
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<td></td>
<td>Dual Ion Chromatography</td>
<td>03-12/2010</td>
<td>20%</td>
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<tr>
<td><strong>150 mm quartz filters for PM$_{10}$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HULIS, levoglucosan</td>
<td>High Performance Liquid - Mass Spectrometry - Mass Spectrometry (HPLC-MS-MS)</td>
<td>01-12/2010</td>
<td></td>
</tr>
<tr>
<td>EC, OC, WSOC, HULIS</td>
<td>Thermal-Optical Carbon Analyzer</td>
<td>01-12/2010</td>
<td>30%</td>
</tr>
</tbody>
</table>

Table 1. An overview of collected filters, analytical methods and studied parameters. The uncertainties were calculated as 2 x standard deviation on replicate measurements, including uncertainty on sampling and analyses.

CONCLUSIONS

HULIS was identified in all 12 analysed samples with higher abundances during winter - early spring (except for one summer week 28) and thus following the Arctic haze period (Figure 1). The mass spectra of HULIS showed the typical odd peak maxima with the 14, 16 Da spacing pattern reported in previous studies (Kiss et al., 2003; Pavlovic and Hopke, 2012). Analysis of selected functional groups of HULIS including carboxylic acids, aromatic carboxylic acids and organosulfates also followed the Arctic haze pattern with elevated winter concentrations. The average molecular weight (AMW) of HULIS was calculated from the MS spectra as described in Kiss et al. (2003). A range from 337 - 392 Da was found for AMW of HULIS with higher molecular weight during summer, possibly due to the role of photochemistry and the seasonal difference in HULIS sources.
Figure 1. Background subtracted total ion current mass spectra (1.2 - 4.5 min) of HULIS in selected Arctic samples (“W” = “Week”). The sample spectra were scaled to 1 m$^3$ sampling volume with 100% = 2.25 x 10$^5$ counts per second. The SRFA and NAFA reference spectra were listed with their corresponding concentrations (µg mL$^{-1}$).

Figure 2 shows the seasonal variation of HULIS-C together with other key parameters OC, WSOC, AMW of HULIS and levoglucosan concentrations, which also reflected a tendency of higher concentrations during the Arctic haze period with the exception of AMW as discussed above. HULIS and levoglucosan showed some correlation, which probably indicates biomass burning as a possible source of HULIS in the Arctic.

It was estimated that HULIS-C concentrations ranged from 2-17 ngC m$^{-3}$, with a higher winter (13 ngC m$^{-3}$) than summer average (4 ngC m$^{-3}$). HULIS-C was converted to HULIS concentrations using a mass-to-carbon conversion ratio of 1.9 (Kiss et al., 2002), accounting for approximately 3-16 % WSOC and 0.7-4.1% TSP mass. Finally, an estimate of annual average HULIS concentration of 0.02 ± 0.01 µg m$^{-3}$ was obtained, indicating potential contribution of HULIS to light-absorbing properties of Arctic aerosols.
Figure 2. Temporal variation of organic carbon (OC), water soluble organic carbon (WSOC), humic-like substances - carbon concentration (HULIS-C), average molecular weight (AMW) of HULIS and levoglucosan concentrations during 2010 (“W” = “Week”).

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This work was partly financially supported by the Danish Environmental Protection Agency with means from the MIKA/DANCEA funds for Environmental Support to the Arctic Region. This work was also supported by the Cryosphere-Atmosphere Interaction in a Changing Arctic Climate (CRAICC) Nordic Centre of Excellence (NCoE). We also thank Christel Christoffersen for performing the levoglucosan analyses.

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INTRODUCTION

Trace gases, Biogenic Volatile Organic Compounds (BVOC) and aerosol particles are tightly linked by various chemical and physical processes taking place in the atmosphere and biosphere (Arneth et al. 2010, Carslaw et al. 2010). However, there are a lot of feedback mechanisms in the earth system that are poorly understood and not yet quantified. Kulmala et al (2013) suggested a framework that couples several feedback mechanisms. A study, based on ground measurements from a boreal forest site, proves the existence of the loop. The aim of this work is to investigate the possibility of using satellite borne products for analyzing this feedback loop.

METHODS AND DATA

Figure 1 illustrates the proposed feedback mechanism between increasing CO₂, processes in forest ecosystems, aerosols and radiation. A rise in the atmospheric CO₂ concentration enhances photosynthesis and thus gross primary production (GPP), i.e. the rate at which ecosystems generate their biomass from chemical energy. This relation initiates the whole feedback loop. The first step demonstrates a rise in BVOC emissions caused by increase in terrestrial vegetation. The next step shows that higher BVOC emissions intensify new particles formation, expressed as aerosol optical depth (AOD), which is a measure of absorbed or scattered light by aerosols. The atmospheric aerosol loading influences significantly the diffuse fraction of radiation, which can be seen at step 3. The feedback loop is completed with the positive connection between increased diffuse radiation and GPP.

The data used in this study includes various satellite based observations. The Moderate imaging spectroradiometer (MODIS) onboard Aqua platform was used to get AOD and GPP. The radiation fluxes were obtained from Clouds and Earth's Radiant Energy System (CERES) level 3 data calculated using diurnal data from geostationary satellites. CO₂ concentration is retrieved by Atmospheric Infrared Sounder (AIRS), while formaldehyde (HCHO) is derived from the Ozone Monitoring Instrument (OMI).
measurements. All data points were co-located with the SMEAR II station in Hyytiälä, southern Finland (61° 51' N, 24° 17' E, 181 meters above sea level), corresponding to typical boreal coniferous forest.

RESULTS AND CONCLUSIONS

The satellite-derived parameters were analyzed to show the causal relation between each step. The time period from 2006 to 2009 was chosen according to the availability of data from all instruments that were used. Only summer was considered as photosynthesis is inhibited during winter and thus all the related processes cease. All steps of the loop showed a statistically significant positive correlation. As an example of one of the steps, Figure 2 demonstrates the last step of the loop: the relation between fraction of diffuse radiation and GPP. The data points are averages of 8 days of measurements during the months May-August in 2009. The solid line shows the linear least squares fit and the correlation coefficient is 0.78.

![Figure 2. Gross primary production as a function of the diffuse radiation fraction. The linear least squares fit to the data is shown with the solid line.](image)

The results show that boreal forest serves as a sink of CO\(_2\) as well as a source for aerosol particles. These both mechanisms lead to the mitigation of climate warming as long as there is an increase in forest growth. Our future plans include working with other types of terrestrial ecosystems and quantifying the strength of this feedback. Satellite data provide a good tool for this purpose in places where there are no long datasets of ground-based measurements available.

ACKNOWLEDGEMENTS

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The Role of Highly Oxidized Organics in New Particle Formation

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Abstract. The role of organic compounds in atmospheric new particle formation is still not clear, some studies conclude that they play no role in new particle formation, while others conclude that they are crucial. In the present work we have used quantum chemical calculations to estimate how stable clusters can form different organic compounds. We have chosen three different organic compounds with increasing O:C ratio. Our results indicate that highly oxidized organic compounds can form stable clusters with sulfuric acid. Thus, they may play an important role in new particle formation.

Keywords: Highly oxidized organics, cluster formation, quantum chemistry, sulfuric acid.

INTRODUCTION

Atmospheric new particle is an important source of aerosols and cloud condensation nuclei (1). Is known that sulfuric acid plays a key role in this phenomenon (2). On the other hand, typical atmospheric concentrations of sulfuric acid and water can not explain the observed new particle formation rates, thus some additional compound/s able to enhance the formation of particles are needed.

In the last decade substantial efforts has addressed the identity of the stabilizing compounds involved in atmospheric new-particle formation. Ternary new-particle formation involving base molecules has been one the most studied alternatives to sulfuric acid-water binary mechanism (3-4). Organic acids produced by oxidation of volatile organic compounds (VOCs) have been proposed as key compounds in new-particle formation as well. However, there is no consensus about the participation of these compounds in new-particle formation; some studies conclude that these oxidized VOC are just involved in particle growth (5), while other studies state that they are involved in the very first steps of new-particle formation but not in growth (6).

In the present work we have used quantum chemical methods to study the stability of clusters formed by sulfuric acid and different organic acids (OxdOrg). We have chosen three oxidation products of alpha-pinene with increasing O:C ratio, namely Pinonic acid (PA), 7-Hydroxy-pinonic acid (HPA) and 3-Methyl-1,2,3-butane-tricarboxylic acid (MBTA).
METHODOLOGY

We used a multi-step method developed by our group (7). The geometry optimizations and frequency calculations were performed with the Gaussian09 program (8) using the B3LYP hybrid functional combined with a CBSB7 basis set, and a single-point electronic energy was then calculated with the TURBOMOLE program (9) using the RI-CC2 method and an aug-cc-pV(T+d)Z basis set.

RESULTS

We have calculated the formation free energy of clusters formed by up to two sulfuric acid molecules and up to two organic acids. Figure 1 shows the formation free energy of the hetero-dimer \((\text{H}_2\text{SO}_4-\text{OxdOrg})\) versus O:C ratio of the organic compounds forming the dimer. Formation free energy of the pure sulfuric acid dimer is shown as a reference.

![Figure 1. Formation free energy at 298K of hetero-dimers versus O:C ratio, dotted line represent the formation free energy of sulfuric acid dimer (-7.89 kcal/mol).](image)

As can be seen, MBTA can form really stable clusters with sulfuric acid while HPA hetero-dimers are less stable that sulfuric acid homo-dimers. This is due to an internal hydrogen bond present in the HPA monomer that is broken when the dimer is formed. In the case of PA there is not internal hydrogen bond. In the case of MBTA the presence of tree carboxylic acid groups allow the formation of three hydrogen bonds with sulfuric acid and one internal hydrogen bond.

We also have studied the addition energy of a second molecule of OxdOrg to different clusters. Results are summarized in Figure 2.
We found that for PA and HPA the addition of the second OxdOrg to the clusters is easier as the number of sulfuric acid molecules in the cluster increases, while in the case of MBTA the addition energy is practically the same for clusters with one or two sulfuric acid molecules. Most probably, in the case of MBTA the second organic will be added already when one sulfuric acid is present in the cluster. The calculations show that the formation of homo-dimers of PA and HPA are not favorable. On the other hand MBTA homo-dimers formation energy is relatively close to the formation energy of sulfuric acid dimers.

CONCLUSIONS

We have shown that the PA can form stable hetero-dimers with sulfuric acid, on the other hand, it will need at least one extra sulfuric acid to add a new PA molecule to the cluster. In the case of HPA the presence of an internal hydrogen bond in the monomer, makes the formation of the hetero-dimer with sulfuric acid less favorable. Probably HPA acid will need more than two sulfuric acid molecules in the cluster to be able to add a second HPA molecule. Finally, MBTA, the most oxidized compound studied, can form really stable hetero-dimers. Furthermore, most likely MBTA hetero-dimer will not need any more sulfuric acid to add a second MBTA molecule to the cluster. All these results point to an important role of highly oxidized organics in new particle formation and growth, although due to the high number of different organic compounds present in the atmosphere, further systematic studies are needed to confirm these preliminary results.

ACKNOWLEDGMENTS

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REFERENCES

Soluble aerosols compositions reconstructed from NEEM (Greenland) deep ice core

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5British Antarctic Survey, University of Cambridge, United Kingdom

Keywords: ice core, aerosol, Greenland, NEEM, sulphate.

INTRODUCTION

Aerosols modify Earth’s radiation budget by direct and indirect effect. Among various kind of aerosols, sulphate aerosols can act as cloud condensation nuclei, leading to increase solar scattering that cools Earth’s climate1. To better understand their current and future climatic impact, we can examine the past climate record. Greenland ice core is a useful archive for reconstructing the past atmospheric aerosols in the Arctic region and Northern Hemisphere. Evidence for a coupling of sulphate and climate may lie in the sulphate record from Greenland ice core, but previous analyses of melted ice-core samples have provided only sulphate ion concentrations, which may be due to sulphuric acid. Soluble aerosol (including sulphate aerosol) compositions and the relationship between sulphate flux and temperature changes in Antarctica have been shown (e.g. ref. 2), however, there is few study about compositions of soluble (sulfate) aerosols in Greenland. In order to clarify characteristics of chemical compositions of soluble aerosols deposited in polar environments, we measured constituent elements of nonvolatile particles in the NEEM (Greenland) ice core by the ice-sublimation method2.

METHODS

A total of 68 samples were distributed from NEEM ice core section from 220 to 1727 m. Soluble aerosols were extracted from the samples by sublimation system at Stockholm University (Fig. 1)3. In the -20 °C clean bench, about 1 g of decontaminated sample was pulverized using a clean ceramic knife and placed on a polycarbonate membrane filter with pores 0.45 μm in diameter which was set in a sublimation chamber. This sublimation chamber was set in a -40°C freezer. Dry and clean air with a dew point of -65°C flew through the stainless steel pipe at a rate of 15 L min⁻¹ for 50 hours. After sublimation, nonvolatile particles remained on the membrane filter (Fig. 2). We measured constituent elements and diameter of these particles using JSM-6360LV (JEOL) SEM (scanning electron micro scope) and a JED2201 (JEOL) EDS (energy dispersive X-ray spectroscopy) system at Hokkaido University. To avoid electric charge on the filter and to improve analysis accuracy, the filter was coated with Pt film by magnetron sputtering (MSP-10 MAGNETRON SPUTTER) before SEM-EDS measurement. Each filters yielded at least 300 particles more than 0.45 μm in diameter, whose constituent elements could be determined by SEM-EDS.

We counted as a non-volatile particle when a particle contains O, Na, Mg, Si, Al, S, Cl, K and/or Ca. We also observed C, Cr and Fe on a few occasions, but interpret these peaks as artefacts from the membrane filter (C), sample mounting (Cr) and the stainless steel of the sublimation system (Fe). Other elements are only rarely detected. We calculated total mass of non-volatile particles (μg) in each filter by adding each particle mass. The mass of each particle was calculated basically following ref. 4.

Ion concentrations were measured at University of Bern and University of Cambridge.
CONCLUSIONS

We show compositions of sulphate aerosol (CaSO₄, Na₂SO₄ and the other sulphate salts) from last glacial period to Holocene. Except of gypsum (CaSO₄), most of sulphate salts are secondary aerosols. CaSO₄ is produced by sulphuric acid and calcium carbonate (dust), and Na₂SO₄ is mainly produced by sulphuric acid and sea-salt. The other sulphate salts including K₂SO₄ and possibly (NH₄)₂SO₄ are probably related to biogenic activity.

We divided whole period into 5 stages by focusing on the temperature and age; Late Holocene (LH: 0.9-3.5 kyr BP), Early Holocene (EH: 8-11.7 kyr BP), Younger Dryas (YD: 11.7-12.7 kyr BP), Bølling-Allerød (B-A: 12.7-14.7 kyr BP) and Last Glacial Period (LGP: 14.7 ~ kyr BP). During the cold stage in YD and LGP, CaSO₄ accounted more than 60 % of sulphate aerosols. On the other hand, during the warm stage in LE, EH and B-A, CaSO₄ is less than 40 %. Instead of CaSO₄, the percentage Na₂SO₄ increased. These results reflect high dust concentration in cold stages. The percentage of the other sulphate salts in warm stages (LH, EH and B-A) is higher than that in cold stages (YD and LGP). Since the other sulphate is considered to be related to biogenic activity, this higher ratio reflect increased vegetation in warm stages (e.g. ref. 5).

Results from the calculation of ion balance ([SO₄²⁻]+[NO₃⁻]+[Cl⁻]-[NH₄⁺]-[Na⁺]-[Ca²⁺]), all SO₄²⁻ in LGP and YD should exist as sulphate salt, because concentrations of total anions are lower than that of total cations. On the other hand, concentrations of total anions in Holocene and B-A are higher than that of total cations, which imply that some SO₄²⁻ exist as sulphuric acid. For the next step, we need to estimate how much sulphuric acid exist in Holocene and B-A to clarify the relationship between sulphate salts and temperature changes in the past in the Arctic region.

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INTRODUCTION

Aerosol particles are omnipresent in the atmosphere, and besides directly influencing the radiative balance of the Earth, they play a crucial role in cloud formation (Stevens and Feingold, 2009). Through a variety of microphysical processes aerosol particles influence the albedo, lifetime and precipitation patterns of clouds in what is known as indirect effects of aerosols on climate (Forster et al., 2007). The ability of aerosol particles to act as cloud condensation nuclei (CCN) is strongly linked to their physical and chemical properties, with the most important parameters being CCN number concentration, aerosol critical diameter $D_c$ and hygroscopicity parameter $\kappa$ (Seinfeld and Pandis, 2006).

METHODS

Size-segregated CCNc measurements have been conducted continuously since February 2009 at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) in Hyttijärvi Forestry Field Station in Finland ($61^\circ 50' 50.685''$N, $24^\circ 17' 41.206''$E, 179 m a.m.s.l.) (Hari and Kulmala, 2005). The CCNc in question is a diffusion-type CCN counter, including a differential mobility analyzer (DMA), condensation particle counter (CPC), optical particle counter (OPC) and a saturator unit. CCN concentrations are measured across 30 size channels, with particle diameters ranging from 20 to 300 nm for five supersaturation $S_{eff}$ levels ranging between 0.1% and 1%. Data were analysed up to April 2012, and, following processing and filtering, a total of 29 non-consecutive months of CCNc data are presented. Critical diameter $D_c$ was calculated for each activation spectrum as a mid-point of the fitted sigmoid curve, i.e. 50% of particles activated (Rose et al., 2008). For each pair of $D_c$ and $S_{eff}$, $\kappa$ was calculated according to the EH1 Köhler model using Eq. A30 in Rose et al. (2008). The surface tension of pure water of 0.072 J m$^{-2}$ was assumed. No normalisation of activation spectra took place prior to the curve fitting; therefore, discussion below concerns only the CCN-active fraction of the ambient aerosol.

RESULTS

The median critical diameter $D_c$ for the whole dataset in this study is reported at 75 nm, with the quartiles indicating a range from 57 nm to 105 nm. The median hygroscopicity parameter $\kappa$ for the whole dataset in this study is reported at 0.22, with quartiles indicating a range from 0.15 to 0.36. The median $\kappa$ shows that aerosol in the boreal environment of Southern Finland is less hygroscopic than the global continental and European continental averages, as presented by (Pringle et al., 2010). The lower $\kappa$ is likely explained by the presence of a larger aerosol organic fraction within the aerosol. Agreeing with Birmili et al. (2009), particle hygroscopicity was found to be size-dependent. Comparing $\kappa$ values from several studies, which utilized a similar measurement setup, reveals that ambient aerosol in the boreal environment is more
hygroscopic than in the Amazon rainforest (Gunthe *et al.*, 2009), high alpine (Jurányi *et al.*, 2011) or mountainous forest environments (Levin *et al.*, 2012) (Fig. 1). This comparison amongst sites also reveals that the rate of change of aerosol hygroscopicity with size in Hyytiälä is higher than in three other locations, indicating differences in the species of condensing material and the oxidation and aging processes.

![Figure 1. Relationship between particle dry size (taken as $D_c$) and hygroscopicity parameter $\kappa$ for four different sites.](image)

For each level of $S_{\text{eff}}$, it was discovered that the distributions of $\kappa$ are log-normal, and these distributions exhibit different shapes between levels of $S_{\text{eff}}$. These size-dependent differences in the $\kappa$ distributions do not support the use of a single $\kappa$ value, mean or median, to describe the whole aerosol population.

The biogenic emissions in the boreal environment of Southern Finland make ambient aerosol of >100 nm in diameter less hygroscopic in the spring and summer time, compared to other seasons – the seasonal variation of $D_c$ needed for CCN activation is important to remember when estimating CCN concentrations from aerosol particle number measurements. The participation of biogenic emissions in photochemical reactions is responsible for introducing a diurnal pattern in the behaviour of aerosol hygroscopicity in the spring and summer for particles ~50 nm in diameter. The diminished photochemistry, temperature and biogenic activity in autumn and winter result both in the highest seasonal hygroscopicity of larger ambient aerosol and in the absence of the diurnal trend of $D_c$ and $\kappa$ for particles of any size.

A subset of CCNc data measured in the spring and summer was used to determine the possible effect of atmospheric new particle formation (NPF) on the diurnal behaviour of CCN activation properties, as described by the $D_c$. In the overall seasonal analysis, during spring and summer $D_c$ at $S_{\text{eff}}$ of 1.0% exhibited a minimum around noon for reasons stated above, similar to what can be seen for the days with no NPF (Fig. 2). During the NPF days the variation of $D_c$ is larger, and the diurnal pattern is clearer (Fig. 2). By the time the newly formed particles are expected to grow to 50 nm in diameter (around midnight),
there is no difference in $D_c$ between NPF and non-NPF days. It seems as though the hygroscopicity of aerosol ~50 nm in diameter is more dictated by meteorological, photochemical and emission parameters, rather than by NPF.

Figure 2. Diurnal variation of median critical diameter $D_c$ on 29 spring Type I event (red) and 53 spring non-event (black) days. Shown from 06:00 of the day in question until 05:00 of the following day for $S_{eff}$ of 1.0%. Error bars are 25th and 75th percentiles.

To get an insight into the chemistry of CCN, the dataset was analyzed in parallel with long-term measurements and proxies of various atmospheric constituents in both gas and particle phase. The sulphuric acid proxy (Petäjä et al., 2009) and sulphate measurements by the aerosol mass spectrometer (AMS) both correlated positively with $\kappa$, pointing out the hygroscopic nature of atmospheric sulphur compounds. It was also found that organic mass fraction and concentrations of monoterpenes and isoprene decrease the $\kappa$ of aerosol. Some seasonal differences were discovered in the effects of abovementioned parameters on $\kappa$; however, the effect of these constituents on aerosol hygroscopicity is larger and more important for particles over 100 nm in diameter. Atmospheric nitric acid and nitrate mass fraction were found to decrease $\kappa$; the correlations, however, were poor and inconclusive. It is suspected that the reduced $\kappa$ at elevated nitrate and nitric acid concentrations may be related either to the fact that nitrate may be present in the organic form, or to the features of airmasses.

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OXIDATION CAPACITY OF MONOTERPENES OVER A BOREAL FOREST: TEMPORAL VARIATION AND CONNECTION TO NEW PARTICLE FORMATION EVENTS

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Keywords: New particle formation, NO₃, OH, O₃.

INTRODUCTION

Volatile organic compounds, especially monoterpenes, are emitted in large quantities by boreal forests (Rinne et al., 2009). These compounds are then removed from the atmosphere by oxidation reactions with ozone, or with radicals such as OH and NO₃. These reactions lead to the formation of less volatile species, and to potential condensation. In this way volatile organic compounds can affect the formation and growth of aerosol particles. In this study, the variation of oxidation capacity over a boreal forest in Finland and its connection to new particle formation was studied.

METHODS

The oxidation capacity of the atmosphere can be defined as the sum of the concentrations of the oxidant species multiplied by their corresponding reaction rate coefficients. For monoterpenes (MT), this can be written as in equation (1).

\[
\text{Oxidation capacity} = k_{OH/MT} \times [OH] + k_{O_3/MT} \times [O_3] + k_{NO_3/MT} \times [NO_3]
\]  

(1)

The oxidation capacity of monoterpenes was calculated for a time period from 1996 to 2011 using data measured in the Hyytiälä field station (Hari and Kulmala, 2005). The ozone concentration was measured directly, but the OH and NO₃ concentrations were calculated from proxies. For the OH concentration, a UVB-radiation based proxy adapted from Petäjä et al. (2009) was used. For the NO₃, the production rate was calculated from measured NO₂ and O₃ concentrations. The average lifetime, \( \tau \), of NO₃ was assumed to be 90 seconds during the night, and 5 seconds during the day (Geyer et al., 2001; Vrekoussis et al., 2004). Using a steady-state assumption, the concentration of NO₃ was then calculated by multiplying the production rate of NO₃ by \( \tau \).

In reality, the lifetime of NO₃ is not constant but varies. The results for the concentration of NO₃ could be improved by calculating an upper limit for \( \tau \), as done by Allan et al. (1999). This will be done at a later stage, using measured VOC, NO₂ and H₂O concentrations.

The calculated oxidation capacity was then compared between new particle formation (NPF) event days, and non-events.
CONCLUSIONS

NO$_3$ is a very strong oxidant for monoterpenes, and is mainly present during the night. Because of this, the oxidation capacity is significantly higher during the night compared to daytime values. This can be seen in figure 1, presenting the diurnal and annual variation of the oxidation capacity of monoterpenes.

![Figure 1: The temporal variation of the oxidation capacity of monoterpenes](image)

The daily mean oxidation capacity of monoterpenes differs between NPF event and non-event days. The values are higher during non-event days during all months except for May and September. The higher values might be caused by the events occurring primarily in unpolluted airmass. Polluted airmass, on the other hand, has large NO$_x$ and aerosol concentrations. NO$_x$ are the main source of NO$_3$, so the NO$_3$ concentration is also higher. The high aerosol concentrations, on the other hand, cause a high condensation sink and hence inhibit nucleation. The differences are, however, only statistically significant in March and October. When comparing the oxidation capacity due to only OH and O$_3$, event days have a higher mean oxidation capacity in every month. In this case, the differences are statistically significant in every month, except for July and August.

ACKNOWLEDGEMENTS

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OVERVIEW OF THE BIOGENIC AEROSOLS – EFFECTS ON CLOUDS AND CLIMATE (BAECC) EXPERIMENT

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Keywords: Atmospheric aerosol particles, biogenic aerosol, new particle formation, field observations, active remote sensing, aerosol-cloud-climate interactions.

INTRODUCTION

Atmospheric aerosol particles affect human health in urban environments, whilst on regional and global scales they can affect climate patterns, the hydrological cycle and the intensity of radiation that reaches the Earth’s surface. In spite of recent advances in the understanding of aerosol formation processes and the links between aerosol dynamics and biosphere-atmosphere-climate interactions, great challenges remain in the analysis of related processes on a global scale. Boreal forests, situated in a circumpolar belt in the Northern latitudes throughout the United States, Canada, Russia and Scandinavia, are of all biomes among the most active areas of atmospheric aerosol formation. Aerosol formation and their growth to cloud condensation nuclei sizes in these areas are associated with biogenic volatile organic emissions (BVOC) from trees and soil (e.g. Kulmala et al. 2004, Paasonen et al. 2013).

One of the world’s most comprehensive observation sites in a boreal forest environment measuring atmospheric aerosols, biogenic emissions and an extensive suite of relevant atmosphere-biosphere factors is the SMEAR-II (Station for Measuring Forest Ecosystem-Atmosphere Relations) station in Hyytiälä, Finland. The station has been monitoring biosphere-atmosphere interactions continuously since 1996 and is operated by the University of Helsinki, Division of Atmospheric Sciences, together with the university’s Forest Science Department. The U.S. Department of Energy’s Atmospheric Radiation Measurement (ARM) Program will bring its ARM Mobile Facility to Hyytiälä, joining SMEAR-II for an intensive measurement campaign called “The Biogenic Aerosols -Effects on Clouds and Climate (BAECC) experiment”. The campaign is starting in February 2014.

The BAECC experiment will provide a bridge from a 19-year long SMEAR-II (Hari and Kulmala, 2005) observation record to the impact of biogenic aerosol on clouds, precipitation and climate. This will be achieved by simultaneous observations of precursor vapor emission, aerosol, cloud and precipitation microstructure. This dataset will be used:

(1) to link precursor emissions and aerosol
(2) to link aerosol at the surface to aerosol in the mixing layer and free troposphere, and
(3) to investigate the aerosol indirect effect on clouds and precipitation.
The ARM AMF observations will be supplemented by tower and surface-based measurements of aerosol and precursor gases. During intensive observation periods (IOPs) aircraft observations of aerosol microphysics will be performed. The experiment will also benefit from existing measurements of precipitation provided by the Finnish Meteorological Institute observational network. The dataset will be placed in perspective with the long time series available from Hyytiälä, and utilized in modeling efforts ranging from process models to global climate models, capitalizing on the ability to perform radiative transfer calculations with full closure.

The main goal of the activity is to understand the impact of a biogenic aerosol formation on cloud properties and ultimately on global climate. The specific aims are:

1) to resolve the role of biogenic secondary aerosol formation in cloud processes in warm, mixed-phase and ice clouds over a boreal environment,
2) by utilizing ARMs state-of-the-art active remote sensing together with process-scale modeling, to complete the link between our comprehensive 18-year observational record of aerosol and biosphere-atmosphere interactions to cloud processes,
3) to expand our local observations over larger spatial scales up to the Earth System via a hierarchy of models (emission, aerosol dynamics, atmospheric chemistry, cloud process, radiative transfer, global climate model) and satellite observations.

The main aim of this presentation is to give an update on current status of the project and planning of the measurements to the Nordic audience. The BAecc experiment welcomes gap-filling contributions by the CRAICC community during the intensive observation period as well as collaboration during subsequent data evaluation and integration.

ACKNOWLEDGEMENTS

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Mitigation of Arctic warming by controlling European black carbon emissions (MACEB): the Arctic black carbon

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Keywords: arctic, black carbon, modelling.

INTRODUCTION

Black carbon (BC) is a light absorbing aerosol. It is formed in incomplete combustion of fossil fuels, biomass and biofuels. Absorption is not the only way how BC affects climate. For example, BC particles can change on the radiation balance by deposition on snow which leads to decrement in the snow albedo. This causes heating and accelerates the melting of the snow cover. Arctic areas have already suffered from the global warming and different methods to protect these areas should be studied.

METHODS

One of the main goals of MACEB project is to find the best approaches to mitigate the warming of Arctic climate by different black carbon emission reductions. To achieve this, several model simulations are conducted with the global aerosol-climate model ECHAM5-HAM2 (Stier et al., 2005; Zhang et al., 2012). We implemented a new anthropogenic emission dataset for BC, organic carbon (OC) and sulfur dioxide (SO\textsubscript{2}). These all are derived from the GAINS model output (operated by the International Institute for Applied Systems Analysis, IIASA). Moreover, we introduced into the aerosol-climate model aviation emissions for BC and updated the ship emissions for OC, BC and SO\textsubscript{2}.

A series of simulations has been carried out with different emission scenarios. We use the year 2005 as a reference year and do scenario simulations for the years 2020 and 2030. We use the nudging method for the model, which means that different scenarios are studied applying today’s climatological conditions. We employ four different emission scenarios. The CLEC and CLECC scenarios include all presently agreed policies affecting air pollutant emissions, but CLECC is further designed to keep the total forcing due to long-lived greenhouse gases at 450ppm CO\textsubscript{2} equivalent level by the end of the century via CO\textsubscript{2} mitigation measures mostly targeting the energy production and industrial sectors. The BCadd scenario includes a portfolio of most important measures that could yield the largest reductions in radiative forcing from short-lived climate forcers (SLCFs) at the global scale in 2030. Measures with a relatively small net impact or increase in radiative forcing have been excluded from this portfolio. MTFR implements the maximum reduction potential of aerosol and SO\textsubscript{2} emissions with currently available technologies. In addition to these scenarios, we study how the emissions from Finland and EU-27 countries influence the Arctic climate. This has been done by removing the BC, OC and SO\textsubscript{2} emissions from the area in focus.
RESULTS AND DISCUSSION

We validated the new emissions with many different tests. Fig. 1 shows one example where the old AEROCOM based and the new GAINS based simulation results are compared with measurements from 5 different locations in Finland. We can see that the GAINS based emissions have more clear yearly cycle. This is not surprising, because the GAINS emissions have different sectors and the energy sector is presented on a monthly time resolution. In addition, the residential and commercial (domestic) sector was modified to have a yearly cycle by using the TRACE-P method (Streets et al., 2000). The GAINS yearly cycle seems to be more realistic than with the old emissions, although the summer values are underestimated. Overall, the model tends to underestimate the concentration with both of the emissions datasets. Beside the errors in the models (deposition, transport, etc.) and emission datasets, we have to keep in mind that measurements and simulations are for the year 2007, but emissions datasets are for 2000 (AEROCOM) and 2005 (GAINS).

To smoothen the influence of the model’s internal variability, we conducted 5 years long simulations from 2003 to 2007 (including 6 months spinup). From these results the monthly mean or cumulative fields are calculated. This approach is taken for all simulations. Fig. 2 shows the difference in BC column burden between different scenario and base year 2005. It is quite clear that all the CLEC and CLECC scenarios give quite similar results. It seems that the BC burden in these simulations increases at the Polar region including area from Greenland to Eastern Russia with North-America in between. On the other hand, in MTFR and BCadd scenarios this is not case: values over the whole Arctic are decreasing. When looking at the differences in the emission maps between the scenarios (not shown here), CLEC 2020, CLEC 2030 and CLECC 2020 are quite similar. The
CLECC 2030 scenario also follows same pattern, but it has more emissions in the North America. On the other hand the MTFR and BCadd scenarios are quite similar with each other. The biggest difference between CLEC/CLECC and MTFR/BCadd scenarios is that the emissions from Middle East, India and China are increased in CLEC/CLECC compared to the base year, and decreased in MFTF/BCadd scenarios. Earlier studies show that the surface air concentrations in the Arctic are mostly influenced by the emissions originating from Europe and Russia, whereas the burden
influenced by emissions coming from North America, Europe, South Asia, and East Asia (Chan et al., 2013; Bond et al., 2013, and references therein).

The surface air concentrations in the Arctic are not influenced by the Asian sources, which can be seen in Fig. 3. All the scenarios give quite similar results, except the CLECC 2030 scenario, where the Northern America values are increased. This is an expected result, as in CLECC 2030 the emissions over North America are higher than in the other scenarios. This also means that the snow/ice deposition (not shown here) is not changed significantly over the Arctic region. The influence of BC to snow albedo is driven by the emissions originating from local sources, mainly from Europe and Russia (Bond et al., 2013). The radiative forcing of aerosol is on the other hand changed by increased BC burden caused by the emissions from Asia.

More detailed analysis in terms of different emission sectors and mitigation methods will be presented at the annual CRAICC conference (2013).

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VOC measurements with PTR-MS at urban background site in Helsinki

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Keywords: Volatile organic compounds, PTR-MS, Urban site, Helsinki.

INTRODUCTION

Volatile organic compounds (VOCs) are mostly emitted into the atmosphere from natural sources (Guenther et al., 1995). However, approximately 10 % of the total emissions is caused by human activity, such as traffic and industry. These anthropogenic VOCs effect to the atmospheric chemistry especially at urban areas (i.e. near the sources) and long-lived compounds have also a contribution to VOC concentrations at rural areas, especially outside the growing season when biological activity tends to be only minimal (Patokoski et al., 2014, in press).

Since November 2012 we have measured several VOCs using proton transfer reaction mass spectrometry (PTR-MS, Lindinger et al., 1998) at the SMEAR III which is an urban background station in Helsinki (60° 12’ N, 24° 58’ E, for detailed description see Järvi et al., 2009). Our aim is to study the importance of VOC sources (both biogenic and anthropogenic) in Helsinki by performing flux measurements. It has been already shown (Hellén et al., 2012; Patokoski et al., 2014, in press) that surroundings of the measurement site are a clear source for many VOCs, however, VOC emissions have not been measured directly before and in this abstract we give an overview of our measurements and research goals.

METHODS

The PTR-MS is a highly sensitive technique for real-time measurements of VOCs. It uses hydronium ions (H₃O⁺) to ionize target compounds via proton transfer reaction and quadrupole technique as a mass analyzer. PTR-MS measures with 1 amu (atomic mass unit) resolution, thus isobaric compounds cannot be identified. PTR technique is still one of the most applicable methods to investigate a major part of common VOCs, such as methanol, acetone, isoprene and monoterpenes.

We measured the VOC fluxes using the disjunct eddy covariance-technique (DEC) which is a conventional method to do direct flux measurements (see Rinne et al., 2007). Ambient concentrations of 27 compounds and fluxes of 11 compounds were measured, by turns, every second hour. The flux, calibration and volume mixing ratio calculation procedures for the PTR-MS are explained elsewhere (Taipale, 2011; Taipale et al., 2008).

RESULTS AND CONCLUSIONS

According to our preliminary results for spring 2013 (January–April), clear emissions of M33 (methanol) and M47 (ethanol) were detected. We observed also emissions for M31 (formaldehyde), M42 (acetonitrile), M59 (acetone), M79 (benzene), M93 (toluene) and M107 (o-xylene) but clear cross covariance peaks (indicates how significant a measured flux value is) occurred only occasionally.
However, these measurements have been done mostly during winter when the micrometeorological conditions are usually challenging for flux measurements.

As an example, Figure 1 shows the diurnal cycles of M33 and M93 emissions and the traffic intensity from a highway near the site. The graphs demonstrate well how vehicles are one important source of the anthropogenic VOCs and in future, our aim is to have a better understanding which other processes are producing VOCs in Helsinki and how large are the total emissions in different seasons.

![Graphs showing diurnal cycles of M33 and M93 emissions and traffic intensity.](image)

**Figure 1:** The lefthandside figure describes the median diurnal cycle of M33 flux and the traffic intensity (measured during January–April 2013) and the righthandside figure shows the same for M93.

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COMPARISON OF SPHEROIDAL CARBONACEOUS PARTICLE (SCP) DATA WITH MODELLED ATMOSPHERIC BLACK CARBON CONCENTRATION AND DEPOSITION, AND AIR MASS SOURCES IN NORTHERN EUROPE, 1850-2010

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Keywords: BLACK CARBON, LAKE SEDIMENTS, PAST DEPOSITION, OsloCTM2, BACK TRAJECTORIES.

INTRODUCTION

Spheroidal carbonaceous particles (SCP) are a well-defined fraction of black carbon (BC), produced only by the incomplete combustion of fossil fuels such as coal and oil (Rose and Rippey, 2002). Their past concentrations have been studied using environmental archives (e.g. Wik and Renberg, 1991; Doubleday et al., 1995; Rose et al., 1999) but additionally, historical trends of BC concentration and deposition can be estimated by modelling (e.g. Lamarque et al., 2010; Skeie et al., 2011; Lee et al., 2012). These models are based on BC emission inventories but actual measurements of BC concentration and deposition play an essential role in their evaluation and validation.

METHODS

We use the chemistry transport model OsloCTM2 (e.g. Lamarque et al., 2010; Berntsen et al., 2006; Lund et al., 2012) to model historical time-series of BC concentration and deposition from energy and industrial sources and compare these to sedimentary measurements of SCPs obtained from five lake sediments (with the method described in Rose, 1994 and Rose, 2008) in Northern Europe from 1850 to 2010. To determine the origin of SCPs we generate back trajectories of air masses to the study sites with FLEXPART (Stohl et al., 2005).
RESULTS

Generally, trends of SCP deposition and modelled results agree reasonably well, showing rapidly increasing values from 1950, to a peak in 1980, and a decrease towards the present (Fig. 1). However, there are evident differences in the beginning of the 20th century with the model showing peaking values while the SCPs mostly haven’t even appeared in the record. The most plausible explanation for the divergence is that the BC peak in 1900 depicted by the model represents other forms of BC than SCP and combustion in the energy and industrial sector in the early 20th century did not always reach the temperatures required for the formation of SCPs (1000°C). In addition there is great discrepancy in the magnitudes between the modelled BC deposition and recorded SCP deposition. This is most likely explained as well by SCPs not representing all BC formed by the energy and industry sectors, but only a relatively small fraction.

Figure 1. Observed depositional fluxes of SCP and modelled BC deposition at the study sites from 1850 to 2010. Results are given in milligram per square meter per year (mg m⁻² yr⁻¹). A) SCP depositional flux for the five dated study lakes, B) SCP depositional flux for the lakes in 10 year averages, C) modelled time slice simulations of BC deposition from the industry and energy sectors at the study lakes, D) modelled time slice simulations of all anthropogenic BC deposition at the study lakes. The model results for 1850 to 1900 are linear interpolations. The SCP deposition results are also linear interpolations between dated observations. Note that the Y-axes are not the same in all panels.

The SCP results show between the sites differences in deposition magnitude that are not captured by the model, but which may be explained by different air mass transport to the sites. According to back trajectories of air masses it seems that trends in SCP deposition to the study sites are not caused by changes in general air mass transportation patterns, at least not during the last 25 years. On the contrary,
differences in observed magnitudes of SCP deposition seem to be caused by differing quantities of polluted air masses being transported to the sites from nearby major emission sources (iron mine in Kiruna and a smelter in Nikel).

CONCLUSIONS

Our study also points to the fact that models might easily miss quite significant regional variation in BC concentrations and deposition both due to the coarse resolution of the model, and possibly underestimation of local emission sources. Our results underline the fact that significant variation in BC results can be recorded within a small geographical area. The concentrations, deposition and trends of BC may vary at a specific site for many reasons. These include factors that are captured by the OsloCTM2 model, but also local conditions that affect the sediment records ability to catch atmospheric deposition that the model cannot account for, and variation in transport patterns of air masses to the study sites. Therefore numerous observational records are required to credibly validate and improve models. While ice sheets are extremely valuable as archives of atmospheric pollutant deposition histories, they are only found on very restricted areas. Lake sediments can be found almost anywhere around the world and can play an important role in recording deposition history of BC and other pollutants.

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ELEMENTAL CARBON CONCENTRATIONS AND DEPOSITION 1700-2004 AD IN AN ICE CORE FROM SVALBARD

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Keywords: BLACK CARBON, ICE CORES, ARCTIC, DEPOSITION.

INTRODUCTION

First continuous measurements of atmospheric black carbon (BC) concentrations in the Arctic started in the late 1980s (Quinn et al., 2011). Despite the significance of BC in Arctic climate warming and geophysical processes, knowledge on its concentrations and climate effects in the area beyond the observational data is scarce. McConnell et al. (2007) were the first ones to report BC deposition trends in the Arctic from two ice cores from the Greenland ice sheet. They found a seven-fold increase in BC concentrations from 1850, peaking around 1910, followed by a decline to almost pre-industrial levels after 1950. However, McConnell et al. recognized that the BC deposition at the high-altitude ice cores sites could not be taken as representative of overall BC trends for lower altitude regions of the Arctic. Hirdman et al. (2010a) confirmed that the source regions of BC for Summit on the Greenland ice sheet, were representative only for this specific site and did not reflect the low-level atmospheric transport of pollution (Stohl, 2006) from high latitude Eurasia that influences much of the rest of the Arctic (Quinn et al., 2011). Therefore, in order to get a better overall view on its trends and effects, further investigations on BC deposition are required from other locations in the Arctic.

Here we present the first results on BC, here elemental carbon (EC), concentrations and deposition on a Svalbard glacier, Holtedalhoffonna, from 1700 to 2004. EC records from Svalbard are of particular importance due to its remoteness from large emission sources and because the Greenland ice cores left the effects of European and even Asian emissions on EC deposition in the Arctic unresolved to a large extent (McConnell et al., 2007).

METHODS

Holtedalhoffonna is the largest ice field on western Spitsbergen island (Svalbard, Norway) covering ca. 300 km\textsuperscript{2} and is situated 40 km northeast from Ny Ålesund research station. A 125 meter deep ice core was drilled in April 2005 at 1150 m altitude at Holtedahlfonna (13°16'20"E and 83 79°8'15" N). The samples were retrieved in ca. 50-60 cm core pieces and immediately packed into clean plastic bags, stored frozen and transported to cold room facilities.
The ice core was cut into parallel-sided sections in a cold room (-22°C) using a thin blade band saw. The pieces where split between tritium, oxygen isotope, organic contaminant and ion measurements. Originally, no section was assigned for EC measurements, but they were performed as a matter of opportunity with ice that was not used for its original purpose. The prism that was used for the EC analysis was originally intended for ion and dust concentration measurements. It was always cut out of the inner part of the core, i.e. the best preserved from contamination generated during drilling and handling of the ice, and therefore excellently fitted the requirements for BC analysis.

The samples for EC analysis were prepared in February 2013 at NPI, Tromsø. The ice samples were melted in cleaned glass jars in a microwave oven with low power in order to prevent any evaporation. The melt water was immediately filtered through pre-burned (at 550°C for 4 hours) quartz fiber filters (Munktel, 5.5 cm diameter) using a hand-pump. All parts of the melting and filtering system were carefully washed and rinsed with distilled water between samples. The filters were left to dry in sterile petri dishes in a cleaned cup board overnight and wrapped individually into aluminum foil in order to avoid contamination between filtering and analysis. Blanks (6) were prepared by placing a pre-combusted filter in the filtering system for a minute. Some blanks (2) were also prepared by filtering distilled water through a pre-combusted filter.

The filters were analyzed for apparent elemental carbon using a thermal optical method (TO, Sunset Laboratory Inc., Forest Grove, USA, [Birch and Cary, 1996]) at ITM, Stockholm University. The analysis was performed with the latest recommended thermal sequence EUSAAR2 (Cavalli et al., 2010) in order to separate EC and other (carbonate and organic) carbon from the filters.

**PRELIMINARY RESULTS**

The EC concentrations in the Holtedahlfonna ice core have varied significantly between 1700 and 2005 (Fig. 1). In the preindustrial era, from 1700 to 1830, the concentrations were generally low, on average 26 µg/L, ranging between 10-45 µg/L. Unfortunately, there were no ice samples left for the 1830-1895 period. Between 1895 and 2004 the concentrations seem to generally be higher than the samples from the pre-industrial period, on average 42 µg/L, ranging between 15 and 96 µg/L. Since 1895 there are also some apparent trends in the EC concentrations. Peak concentrations were measured around 1910 and 1940 (73 µg/L and 58 µg/L, respectively). The EC concentrations are steadily increasing from around 1970 to 2004, with highest values of the whole core recorded in 1998 (96 µg/L). The lowest concentrations during the 1895-2004 period were observed in 1920s and beginning of 1970s.

![Figure 1. Elemental carbon (EC) concentrations measured from a Holtedahlfonna ice core with a thermal-optical method. The black line represents 5-year running means.](image)

The magnitude of the recorded EC concentrations is in accordance to previous studies using a comparable method to measure EC in ice cores from the European Alps (Lavanchy et al., 1999; Jenk et al., 2006; Legrand et al., 2007). The concentration trend in the ice core from Holtedahlfonna shows some similarities to
the trend recorded in Greenland ice cores which show a peak in the early 1900s and a decrease afterwards, although these concentrations were measured with a different method (McConnell et al., 2007).

The most surprising feature of the Holtedahlfonna ice core record is the apparent increase in EC concentrations since around 1970. This rise is unprecedented in any European or Arctic ice core. It also seems to contradict atmospheric BC measurements from the Arctic, with all measurement stations, Alert, Barrow and Zeppelin, indicating decreasing atmospheric BC concentrations since the beginning of the observations in the end of 1980s (Hirdman et al., 2010b).

EC concentrations in an ice core are affected by numerous factors related to processes both around deposition and after deposition such as the snow accumulation and meteorology at the site. Therefore, in order to illuminate the reasons for trend in the recorded EC concentrations, we calculated the deposition of EC at the ice core site, i.e. the deposition of EC particles on a square meter of ice surface per year. Dating of the ice core was performed using an age-depth scale based on the Nye thinning model (Nye, 1963) constrained by the depth of the 1963 radioactivity fallout layer at 28.5 m depth (van der Wel et al., 2011). In addition, a dating method based on statistical extraction of historically known volcanic eruptions (Moore and others, 2012) was included here. The deposition trend is shown in Figure 2. It has similarities to the trend seen in the concentrations with lower deposition before the industrial era and high deposition in the beginning of the 20th century. The most evident difference is that the deposition continues to decrease quite constantly until the 1970s from the peak values around 1910. As a consequence it seems that the apparent peak and variation in EC concentrations occurring between 1920 and 1970 might have been partly caused by changes in snow and ice accumulation during this time period rather than more EC being deposited to the glacier.

![EC deposition](image)

**Figure 2.** Elemental carbon deposition to the Holtedahlfonna ice core. The black line represents 5-year running means.

Strikingly, the rapid increase in EC values seen in the concentrations is still apparent in the deposition fluxes since the 1970s. This indicates that more EC has been deposited at the site from 1970 towards the present despite decreasing measured concentrations in the atmosphere (Hirdman et al., 2010b). One possible explanation for this discrepancy could be the different methods used for the measurement of EC in the atmosphere and in the ice.

**CONCLUSIONS**

Work is continuing to disentangle the cause of the increasing EC concentrations and deposition suggested by the ice core from Holtedahlfonna. We have ruled out the contribution from any local sources, since measurements of EC in snow around Ny Ålesund settlement have shown the local concentrations to represent general arctic background levels (Aamaas et al., 2011). One possible explanation and an explanation under investigation is changes in the cloud scavenging of EC. Back trajectory modelling is carried out for the coring site in order to find out the source areas for EC. Black carbon emissions have
decreased or stayed constant in Europe and North America, which are the most likely source areas, for the last decades. However, the emissions from China, India and partly the former USSR have increased during the same time (Bond et al., 2007). Therefore the present results might indicate some long-range transport of EC reaching Svalbard and Holtedahlfonna.

Regardless of the cause for the increasing EC values, the results have apparent and significant implications to the radiative transfer of the coring site. Modelling of the past radiative forcing of EC in the Holtedahlfonna area is possibly going to be conducted based on the present results.

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ON THE TEMPERATURE DEPENDENCE OF SEA SPRAY AEROSOL GENERATED USING A LABORATORY PLUNGING JET

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Keywords: PRIMARY MARINE AEROSOL, BUBBLE BURSTING.

INTRODUCTION

Sea salt aerosol (SSA) production by wind and breaking waves is the dominant source of primary marine aerosol mass (Lewis and Schwartz, 2004). SSA production has been related to wind speed using both exponential functions (Nilsson et al., 2001; Geever et al., 2005) and power law functions (e.g. Mårtensson et al., 2003) via white cap cover ($W$) functions (e.g. Monahan and O’Muircheartaigh, 1980; Monahan et al., 1983). Aside from wind speed a number of other parameters are thought to be important in the process of SSA production. These include sea surface temperature ($T_w$), sea ice coverage, salinity ($S$), ocean wave field, and the organic composition of seawater (especially surface-active organics).

Monahan and O’Muircheartaigh (1980) were the first to consider a role for $T_w$ in SSA production. They devised the most commonly used expression relating the white cap coverage to wind speed:

$$W = 3.84 \times 10^{-6} \times U^{3.41}$$ (1)

where $U$ is the wind speed at 10 m. The data behind this model were obtained almost entirely in the sea surface temperature range 20°C to 30°C and the authors noted that upon later inclusion of data obtained in the sea surface temperature range 12°C to 14°C the model fit changed significantly; $W$ increased for this lower temperature range especially at lower values of $U$. Monahan et al. (1983) came to similar conclusions when they considered a model based upon data obtained during the JASIN 1978 expedition:

$$W = 5.4325 \times 10^{-6} \times U^{3.31}$$ (2)

This model results in ~20% higher values of $W$ at 5 m s$^{-1}$, ~5% higher at 20 m s$^{-1}$, asymptotically approaching ~0% at higher wind speeds when compared to Equation 1. Monahan and O’Muircheartaigh (1980) speculated that the reason for this difference was the effect of $T_w$ on the rise velocity of bubbles in seawater ($V_B$) and the resulting effect on the lifetime of white caps: from earlier observations it was known that the lifetime of whitecap foaming ($L$) was dependant on $T_w$ (Miyake and Abe, 1948). Their laboratory experiments produced a rather strong dependence:

$$L \approx \exp \left( -T_w / 25 \right)$$ (3)

More recent work has identified significant non-linear negative correlations between SSA number production and $T_w$ in all sizes from 0.02 µm to 1.8 µm $D_d$ (Hultin et al., 2011; Zábori et al., 2012a,b). It has also been noted that there is a clear difference in the temperature effects on SSA production seen between those experiments deploying glass filters/diffusers (e.g. Mårtensson et al., 2003; Sellegrí et al., 2006) and those using plunging water jets (e.g. Hultin et al., 2011; Zábori et al., 2012a,b). The latter exhibit a similar response to that seen by Bowyer et al. (1990) (likely
due to the type of plunging wave generated in this tank experiment) with larger decreases in SSA production, no effects at higher temperatures and no positive correlation below $\sim 2\mu m D_d$. These recent experiments suggest that the links between $T_w$ and SSA production are likely to be physical in nature; effects are noted independent of whether real or artificial seawater is used, are independent of salinity (so long as the water is not completely fresh) and are independent of the organic content of the water. There do however appear to be differences between experiments operating at steady state and those testing dynamic temperature changes. For this reason a system on a similar scale to those of Hultin et al. (2011) and Zabori et al. (2012a,b) with improved temperature control over long time periods may offer significant insight into the physics of the system. It is also clear that we need a new temperature dependent source parametrisation that incorporates these new experimental results. As such these were the objectives of the current study.

METHODS

In order to constrain the effect of water temperature on sea spray aerosol generated using a laboratory plunging jet a new high-capacity sea spray simulator (ISS) was constructed. The system was fabricated from stainless steel components and consisted of a jacketed stainless steel vessel design. The jacket section of the vessel was plumbed to a temperature controlled ($\pm 0.1 \text{ K}$) water circulating bath. In order to avoid leaching of organics from moving parts, seals, and glands a peristaltic pump was used to generate the plunging jet by pumping water from the centre of the tank bottom back through the centre of the lid. Here a stainless steel nozzle with inner diameter 4 mm held in a vertical position 35 cm above the air–water interface inside the tank was used as the exit for the plunging jet. All surfaces on the inside of the tank were coated in PTFE and all tubing in contact with sample water was silicone. A series of ports were added to the side and top of the tank to obtain water and air samples respectively. Aerosol laden air was sampled through a port in the lid of the sea spray simulator and transferred under laminar flow to all aerosol instrumentation.

A GRIMM 1.109 Optical Particle Counter (OPC) was used to measure particles in the range $D_p > 0.25 \mu m$ at 1 Hz. The aerosol size distribution for the size range $0.25 \mu m < D_p < 32 \mu m$ was determined every 6 s, sizing particles in 31 bins. The total number concentration was measured at 1 Hz for particles with $D_p > 0.01 \mu m$ using a TSI model 3010 Condensation Particle Counter (CPC). The size distribution for the size range $0.01 \mu m < D_p < 0.41 \mu m$ was determined using a closed-loop sheath air custom-built differential mobility particle sizer (DMPS) equipped with a TSI 3772 CPC. A single scan over 34 size bins was completed in 11 minutes.

The bubble size distribution at the water surface (sometimes referred to as foam) was photographed using a dSLR Pentax K-7 digital camera equipped with a Pentax SMC-D FA 100 mm f/2.8 macro lens at 60 s intervals, 40 cm above the water surface, $\sim 10 \text{ cm}$ from the centre-line of the plunging jet. The bubbles were backlit by placing a Pentax AF-540 FGZ flashlight adjacent to a submerged viewing window. This arrangement provided enough light near the water surface to distinguish the bubbles against a dark background. The 60 s interval was chosen to ensure that the same bubbles were not accounted for more than once in subsequent image analysis. The camera captured 4672 X 3104 pixel images representing a 93.8 mm X 61.1 mm section of the water surface (based upon a sensor size of 5 $\mu m$ X 5 $\mu m$ and an empirically derived scaling factor)

Bubbles larger than 30 pixels in diameter along the minor axis (the smallest bubbles reliably detected by eye) were visually identified with a black circle fitted to each one on a transparent layer above the image. A third white layer was subsequently added between these two layers before the image was re-saved with its original dimensions. Finally a MATLAB based program was developed to automate the analysis of the greyscale processed images returning a matrix of bubble sizes identified in the processed images.

A series of experiments were conducted where all parameters aside from the water temperature were
held constant. The water temperature was varied in the range $-0.4\, ^\circ\text{C}$ to $25.3\, ^\circ\text{C}$ in increments of $\sim 0.4\, ^\circ\text{C}$ in the range $-0.4\, ^\circ\text{C}$ to $8.1\, ^\circ\text{C}$ and in increments of $\sim 5\, ^\circ\text{C}$ thereafter. For each experiment the temperature was held constant for $\geq 6.4\, \text{h}$. Each experiment was conducted with artificial seawater (ASW) consisting of sea salts (Sigma Aldrich, S9883; 55\% Cl, 31\% Na, 8\% SO\textsubscript{4}\textsuperscript{2–}, 4\% Mg, 1\% K, 1\% Ca, <1\% other) rehydrated to an absolute salinity of $35\, \text{g\,kg}^{-1}$ using low-organic-carbon type 1 deionised water ($>18.2\, \text{M}\Omega$; DIW).

CONCLUSIONS

Mean particle number concentrations for $D_p > 0.01\, \mu\text{m}$ decreased non-linearly with increasing $T_w$ in a manner similar to previous studies (Zábori et al., 2012a, 2013). Although particle number concentrations decreased across the full range of temperatures measured, most of the decrease (a factor of $>2.5$) occurred in the range $-0.5\, ^\circ\text{C}$ to $10\, ^\circ\text{C}$ (Figure 1). No significant differences in aerosol size distribution were identified with changing temperature.

The total number of bubbles ($D_b > 400\, \mu\text{m}$) in the images of the water surface exhibited a similar relationship with water temperature and a correlation between the mean particle number concentration ($D_p > 0.01\, \mu\text{m}$) and the number of bubbles at the water surface ($D_b > 400\, \mu\text{m}$) resulted in $R^2 = 0.98$.

![Figure 1: Total particle number ($D_p > 0.01\, \mu\text{m}$), total number of bubbles in the water surface images, and air entrainment as a function of water temperature ($T_w$).](image)

Figure 2 presents surface bubble size distributions obtained from three of the experiments conducted along with subsurface bubble size distributions from a number of previous studies. The distributions are characterised by typical power-law dependence resulting from the cascade of bubble fragmentation. A broad maxima is evident at $\sim 1\, \text{mm}$ which is shifted to slightly larger maxima than previous studies focused on subsurface bubbles. Given that spectra of subsurface bubbles represent a distribution of volumes whilst the data in this study represent bubbles at the air–water interface, a period later in the evolution of the bubble cloud, the data are not in disagreement. Initial inspection of the size distributions obtained at different temperatures during this study suggest that temperature does not shift the bubble size distribution. This leads to speculation that rather than altering the distribution of bubbles, a decrease in $T_w$ leads to an increase in air entrained by
the plunging jet. Figure 1 also plots air entrainment as a function $T_w$ based upon the model of (El Hammoumi et al., 2002). Although this model predicts an increase in air entrainment with lower $T_w$ it suggests a more linear relationship than can explain the observations of total particle number and total bubble number observed in this study. However the data used to derive this model were obtained by simply varying the density, viscosity and surface tension of water through the addition of alcohol, Lobelia oil and glucose. As such it is unlikely to capture physical changes in seawater with changing $T_w$ adequately. This highlights the need to ascertain the dependence of air entrainment in inorganic artificial seawater by plunging jets as a function of $T_w$.

![Figure 2: Bubble size distributions for three temperatures investigated during the experiments. The black line fits show reference power law scalings for bubble distributions. Theoretical considerations lead to a $-\frac{3}{2}$ power law scaling for bubbles larger than the Hinze scale (\sim 1 mm). Bubbles smaller than the Hinze scale are more variable in their power law scaling but roughly follow a $-\frac{10}{3}$ trend (Deane and Stokes, 2002). The thick black curve is data from Loewen et al. (1995).](image)

In summary we provide a new comprehensive dataset of laboratory plunging jet derived sea spray aerosol as a function of temperature in the range $-0.5 \degree C$ to $25 \degree C$. Our data supports previous studies by showing that the size distribution of sea spray aerosol does not shift and only changes in magnitude. We show for the first time that this is due to increased bubble number at the water surface rather than a change in bubble sizes with colder temperatures. This hints that in laboratory seawater plunging jet systems, the dependence of air entrainment is a highly non-linear function of $T_w$ with likely implications for comparison of laboratory plunging jet systems with breaking waves as well as our understanding of changes to the primary marine aerosol source with changing climate.

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INTRODUCTION

Studies show an Arctic amplification to global emissions of black carbon (BC), which absorbs solar radiation in the atmosphere and when deposited on snow (e.g. Hansen and Nazarenko, 2004; Jacobson, 2004; Flanner et al., 2007; Koch et al., 2009). Reduction of BC emissions has been suggested as a short-term climate control strategy (Hansen et al., 2000; Jacobson, 2010; Shindell et al., 2012). In this study we address the question of how sensitive the Arctic climate is to black carbon (BC) emitted within the Arctic compared to BC emitted at mid-latitudes. We consider the entire emission-climate response spectrum and present a set of experiments using the coupled climate model NorESM. A new emission dataset including BC emissions from flaring and a seasonal variation in the domestic sector has been used. The climate model includes a snow model, SNICAR, to simulate the climate effect of BC deposited on snow.

Unlike scattering aerosols that exert a weak (negative) forcing over snow, BC aerosols absorb solar radiation and exert a positive forcing over white surfaces, both in the atmosphere and when deposited on snow. This makes the forcing and the potential impact of BC particularly high in the Arctic during spring, when there are large amounts of sunlight available, most of the surfaces are still covered with snow and sea-ice, and the BC concentrations are at a maximum. Arctic BC originates mostly from source areas outside the Arctic and is a result of a long-range transport from lower latitudes (Law and Stohl, 2007). In the Arctic boundary layer, surfaces of low potential temperatures form a dome over the Arctic. The high static stability associated with strong surface inversions in the Arctic boundary layer suppresses the mixing of pollution and heat from the free troposphere to the boundary layer, and BC reaching the Arctic from lower latitudes is not easily deposited on the Arctic surface.

Several model studies highlight the importance of the vertical distribution of BC in regards to the climate response (Hansen et al., 2005; Ban-Weiss et al., 2012; Flanner, 2013; Samset et al., 2013). Flanner (2013) perturbed BC mass in different altitudes in the Arctic, and found a strong surface warming for BC located near the surface, a weak surface warming for BC at 400-750 hPa and a surface cooling for BC at 210-250 hPa. An earlier study showed similar trends in the sign of temperature change for BC perturbations at the global scale (Ban-Weiss et al., 2012). Previous studies have shown that atmospheric absorption by present-day BC in the Arctic atmosphere (i.e. neglecting the impact of surface deposition) may have a small or even negative impact on the surface temperatures, as most of the BC aerosols are located above the Arctic dome (Shindell and Faluvegi, 2009; Sand et al., 2013). The studies indicate the mitigation strategies for present-day BC should target emissions outside the Arctic. However, potential BC sources within the Arctic dome are more likely to warm the surface due to the near surface solar heating and the greater likelihood of surface deposition.

The boundaries of the Arctic dome are highly variable in time and space, with a maximum extension over Eurasia during winter. Here the snow-covered surfaces make the air sufficiently cold, so that pollution can be transported directly into the high-Arctic boundary layer (Stohl, 2006). Emissions during winter in
Eurasia will therefore have a greater impact on the Arctic climate, highlighting the importance of seasonal differences in emissions.

Current inventory estimates show that the dominant BC emissions within the Arctic today are caused by flaring related to the oil and gas fields in North Western Russia (Stohl et al., 2013). Compared to mid-latitudes, within-Arctic BC emissions are low, but the emissions are expected to grow due to new developments in the Arctic, the opening of the Northern sea routes to shipping, and enhanced oil and gas exploration. The use of wood stoves in the Nordic countries, Russia, Canada and Alaska during winter is one example of emissions in the domestic sector that have a large impact per unit emission in the Arctic. These emissions are expected to increase.

As the model studies of Shindell and Faluvegi (2009), Sand et al. (2013) and Flanner (2013) focused on the local climate response to local BC forcing, the studies are less relevant for policies that focus on mitigation of BC emissions at high latitudes. In this study we want study the climate effect of emitting BC in different regions. We investigate how anthropogenic BC emissions within-Arctic or from mid-latitudes influence the Arctic climate, both through absorption in the atmosphere and through changes in surface albedo when BC is deposited on snow and sea-ice. The scientific questions we want to address are: 1) How different will the Arctic climate response to BC emissions be if BC is emitted within the Arctic, compared to if BC is transported from lower latitudes and 2) how much of the BC forcing and response in the Arctic can be attributed to BC deposited on snow and sea-ice?

METHODS

In this study we have used a coupled Earth System model, NorESM, together with a snow model, SNICAR, to include the effects of BC deposition on snow and ice. A new emission dataset has been used for BC that includes BC emissions from flaring, and a seasonal variation in the domestic sector, to account for amplified use of wood stoves during the cold season. The model is run on a 1.9°×2.5° horizontal grid with 26 vertical layers in the atmosphere. The climate simulations have been run for 60 years from a 140 year spin-up with the same 2008 emissions and greenhouse gas levels. The last 30 years have been used for analyses. The climate simulations include one control run, four perturbed runs with BC emissions scaled up north of 60°N, and in the mid-latitudes (28-60°N), respectively. To distinguish the climate impact of BC deposited on snow and sea-ice, the two perturbed runs have been repeated without any impact of BC deposited on snow and ice.

CONCLUSIONS

We find that BC emitted within the Arctic has an almost 5-times larger Arctic surface temperature response (per unit of emitted mass) compared to emissions at mid-latitudes. Especially during winter, BC emitted in North-Eurasia is transported into the high Arctic at low altitudes. A large fraction of the surface temperature response from BC is due to increased absorption when BC is deposited on snow and sea-ice with associated feedbacks. Today there are few within-Arctic sources of BC, but the emissions are expected to grow due to increased human activity in the Arctic. There is a great need to improve cleaner technologies if further development is to take place in the Arctic, especially since the Arctic has a significantly higher sensitivity to BC emitted within the Arctic compared to BC emitted at mid-latitudes.

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GHG EXCHANGE AND THE CARBON CYCLE IN AN ARCTIC COASTAL AREA

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Keywords: ATMOSPHERE-SURFACE EXCHANGE, AEROSOL FORMATION, CLIMATE CHANGE.

INTRODUCTION

Emissions of carbon containing substances like CO₂, CH₄ and VOCs including DMS from marine and terrestrial surfaces have a climate impact through formation of aerosols or directly as greenhouse gas (GHG). Diminishing of sea ice is expected to have a direct and indirect effect on the exchange of these carbon containing compounds over terrestrial as well as marine areas (Parmentier et. al. 2013). However it is still not known to which extent the diminishing ice will affect the exchange; thus it is of urgent concern to obtain knowledge of the processes and parameters controlling the exchange. In a joint collaboration between Aarhus University, University of Manitoba and Greenland Climate Research Centre we will study these processes in the Young Sound area in North East Greenland, in order to be able to quantify the effect of diminishing sea ice on the GHG and aerosols.

METHODS

In the proposed project we will examine and quantify to what extent the changing sea ice condition affects the carbon cycle and surface fluxes over different surfaces (terrestrial/marine) within and adjacent to high Arctic Young Sound fjord system, and how these systems are inter-connected. Sea ice influences the temperature in the Arctic; thus we will examine to what extent temperature influences the carbon systems and the surface flux of carbon, and other climatically important gases within this coastal regime. Furthermore we will study the atmospheric transformation and aerosol formation processes which are affected by emissions from the ecosystems. Knowledge of the processes and interactions described above is important in order to develop up scaling parameterizations or ecosystem models, which can be used to quantify the effect of diminishing sea ice on the GHG and aerosol concentrations.

Specific questions we will address are:
- How do the exchange velocities over cold coastal water surfaces respond to both weather and sea ice.
- How do ecosystem processes, controlling the surface exchange, respond to both weather and sea ice?
- Will a warmer surface (soil or ice) lead to higher exchange velocities and enhanced exchange?
- What are the main sources of the Arctic aerosols?
- Which parameters in terms of atmospheric gases, humidity, temperature etc. are controlling the atmospheric particle formation?
- To what extent does emission of VOCs, including DMS from Arctic ecosystems affect formation of atmospheric particles?

Measurements of surface exchange, atmospheric composition (gases and aerosols) and stratification and ecosystem parameters will be carried out at Zackenberg, Daneborg and Station Nord. Field work and data collection will start in early spring 2014 in Zackenberg and Daneborg and last until fall 2014. Similar measurements will take place at Station North starting in early spring 2015.

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LIGHT ABSORBING AEROSOL IN LIQUID DETECTED WITH THE SINGLE PARTICLE SOOT PHOTOMETER

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Keywords: Black Carbon, Albedo, Single particle soot photometer

INTRODUCTION
Absorbing aerosols, with Black Carbon (BC) being one of the most recognized species, have for a long time been known to modify the climate in different ways (e.g. Hansen & Nazarenko, 2004). One key aspect is once the aerosol is deposited onto snow surfaces, in which the albedo of the snow surface is drastically reduced. This has been suggested to lead to perturbations in the radiative balance in regions such as the Himalayas and the Arctic (Flanner et al., 2007).

In the three measurement techniques used today to determine BC in snow, only one has the ability to measure the size distribution. An instrument with this ability is the single particle soot photometer (SP2), and the recent works by Schwarz et al. (2012, 2013) were the first studies to present size distributions of BC in snow samples. Previously, the SP2 had only been utilized to determine BC concentrations in ice and snow (e.g. McConnell et al., 2007; Kaspari et al., 2011). The size of BC particles in snow is of interest since it will affect BC’s light absorption in snow. From the work of Schwarz et al. (2012, 2013) it appears that BC particles exist in larger sizes in snow compared to typical BC particles in the air, suggesting a reduction of BC’s absorption in snow. More measurements and developments of the measurement technique are necessary to confirm these observations. The aim of this work is to present the measurement developments of BC in liquid (including size distributions), which will be used for snow samples collected in the Scandinavian Arctic.

METHOD
The SP2 was used to quantify the refractory BC mass through laser-induced incandescence (Stephens et al, 2003). Since the SP2 measures ambient aerosol an ultrasonic nebulizer (U5000AT+, Cetac) is needed to aerosolize the particles when measuring particles in a liquid. This additional step introduces further uncertainties in the measurements and has been proven to be system set-up dependent (Schwarz et al., 2012). The measurement set-up and the consequent nebulizing efficiency in this work were examined through an empirical approach, similar to the procedure in Schwarz et al. (2012).

Since different sized particles were aerosolized with different efficiencies we used polystyrene latex sphere (PSL) concentration standards with diameters of 100, 202, 304, 360, 498, 802, 1112, and 2010 nm to carefully determine the size dependence on the nebulizing efficiency. The efficiency at which particles were nebulized and detected by the SP2 was also shown to be dependent of the peristaltic flow rate supplying the ultrasonic nebulizer. The flow with the highest efficiency was the range of 0.02-0.04 mL min⁻¹, where the average nebulizing efficiency for all PSL sizes was 0.017. Figure 1 shows the nebulizing efficiency for each PSL size tested in this study. With the known efficiency for the PSL’s it was assumed that the stopping distance was the same as BC particles, thus connecting the PSL nebulizing efficiencies to BC particles. Different concentrations of Aquadag (standard BC material used to calibrate the SP2) in H₂O (2 ng g⁻¹ to 800 ng g⁻¹) were thereafter measured with the SP2 using the same exact set-up as the PSL’s. The size dependent efficiency curve (based on the PSL’s) was then applied to the different gravimetric BC solutions to scale them to their corrected BC concentration.

CONCLUSIONS
The gravimetric samples have a good agreement with the BC concentrations detected by the SP2 based on the adjustment according to the size dependent PSL nebulizing efficiency (figure 2). The mass size distribution showed to be reasonable in the size range where the particles are aerosolized with the measurement set-up used in this work.
ACKNOWLEDGEMENTS

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TRENDS IN CRITICAL ICE SUPERSATURATION FOR DEPOSITION NUCLEATION

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Keywords: ICE, NUCLEATION, DEPOSITION, CIRRUS

INTRODUCTION

A primary objective of the CRIACC work package five (WP5) is to contribute detailed scientific understanding to the interrelation of clouds, aerosols, and climate in the Arctic environment. In Arctic and Nordic environments ice nucleation efficiency and growth morphology will affect cloud lifetime and radiative properties, with implications for water cycling and global climate. Here we report on ice formation by water deposition on climate relevant substrates with a range of hydroscopic behavior. Ice nucleation and growth morphology are probed using helium and light scattering techniques at temperatures up to 213 K. The results are examined in the context of classical nucleation theory.

EXPERIMENTAL METHOD

Deposition nucleation experiments were performed using an environmental molecular beam (EMB) apparatus (Kong et al., 2011; Kong et al., 2012) that focuses a low density beam of molecules onto a graphite surface. The surface is housed within an environmental chamber that allows finite vapor pressures ($\leq 10^{-2}$ mbar) to be sustained. Thus in addition to the graphite, organic layers in dynamic equilibrium with their vapor can be condensed and used as ice nucleating substrates. The technique differs critically from other UHV systems in that it allows surfaces under atmospherically relevant temperatures and pressures to be directly probed.

Surface coverage and nucleation on the substrate is monitored with a molecular probe of He atoms that is efficiently attenuated by ad-layers. Ice nucleation on layers of vapour-deposited substrate is directly monitored using the surface reflections of a 670 nm laser. A surface roughness model is used to estimate surface morphology based on the attenuation of the scattered light signal (Kong et al., 2012).

The molecular flux and thus water vapor pressure within the chamber is measured using a rotatable quadrupole mass spectrometer (QMS). This allows the supersaturation required for ice nucleation to be determined as a function of temperature and surface properties.

RESULTS AND DISCUSSION

We observe that the nucleation of ice on a bare graphite crystal becomes increasingly inefficient as the surface temperature decreases from 200 to 155 K. The supersaturation over ice required for nucleation to occur increases from 130\% at 200 K to 850\% at 155 K. Adsorption of vapour deposited layers on the graphite surface affects the surfaces hydrophilicity and thus the required
supersaturations for nucleation. For each tested compound the supersaturation required for nucleation increases rapidly with decreasing temperature in the range 160-190 K. Although the specific ice nucleation efficiency is compound dependent the trends with temperature are comparable, and are also consistent with literature data in the 150-200 K range. Thus the hydrophilicity of the surface influences the absolute nucleation rate, but the overall trend with temperature is qualitatively similar for the different systems. We employ classical nucleation theory in a search for a quantitative physical description of the observed deposition behavior. The implications for the description of heterogeneous ice nucleation in the upper troposphere and lower stratosphere are discussed.

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THE SOURCES AND INFLUENCE OF AEROSOLS IN THE ARCTIC ON GLACIER ENERGY BALANCE

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Keywords: GLACIER MELTING, AEROSOL SOURCES, AEROSOLS.

INTRODUCTION

The project focuses on the source mechanics and impact of deposition of airborne aerosols (dust, volcanic ash, and black carbon) on the glacier surface albedo and possible consequences for the future climate evolution in Arctic regions.

Albedo changes related to snow/ice impurities in Iceland (Figure 1) are likely driven by deposition of dust in normal years (Thorsteinsson et al., 2011a), sometimes possibly by wildfires (Thorsteinsson et al., 2011b), and by deposition of volcanic ash after major eruptions, such as the 2010 eruption of Eyjafjallajökull (Thorsteinsson et al., 2012) and Grímsvötn 2011.

During and after the subglacial eruptions in the subglacial Eyjafjallajökull volcano 14 April to 22 May 2010 and Grímsvötn volcano 21 to 28 May 2011, tephra was blown over all the major ice caps in Iceland. After the 2010 eruption, the entire Eyjafjallajökull ice cap and most of the neighbouring Myrdalsjökull, were covered with a thick ash layer which insulated the ice and snow surface from atmospheric energy fluxes (Figure 2a), whereas, in contrast, a thin tephra layer on the three largest ice caps in Iceland (Vatnajökull, Hofsjökull and Langjökull) significantly increased the shortwave radiation flux entering the glacier (Figure 2b). Similar contrasting conditions were observed after the 2011 eruption of Grímsvötn in Vatnajökull.

METHODS

The study will make use of data collected from glaciers in Iceland during the summers since mid-1990’s. The mass balance has been observed at 40-60 sites on Vatnajökull since 1992 and at 22-23 sites on Langjökull since 1996. During the summers since 1994 automatic weather stations (AWSs) at 2-10 locations on Vatnajökull and 2-3 stations on Langjökull (since 2001), have monitored at 10 minutes interval all the meteorological parameters needed to calculate the glacier surface energy balance. The data include field observations of glacier surface albedo during the summer on 8-10 automatic weather stations on Vatnajökull ice cap and 2 stations on Langjökull ice cap, both shortwave and longwave radiation balance, as well as data to estimate the turbulent heat fluxes of the atmospheric boundary layer (vertical profiles of temperature, wind and humidity) as well as the consequential ablation and measured glacier runoff (e.g. Björnsson et al., 2005; Güdmundsson et al., 2009).

The aim is to describe the dust and ash dispersion and the effects on snow and glacier melt. The field observations include: a) both incoming and outgoing shortwave and longwave radiation balance, b) data to estimate the turbulent heat fluxes of the glacier boundary layer, c) the specific mass balance observed in-situ at location of stakes, d) time series of digital elevation maps, and e) glacier runoff. Time series of field data from the glaciers in Iceland show a wide range of impacts of albedo changes on glacier melting.

The project will also make use of data collected in Sodankylä on snow albedo, in particular during the SNORTEX experiments, and data from dedicated CRAICC experiments on the deposition of black carbon and ash on snow and it’s effects on snow albedo and snow melt.
Satellite observations of glacier surface albedo (~5 km spatial resolution at daily to weekly temporal resolution) will be calibrated and verified by ground based observations of albedo.

With FLEXPART, the project has a model at its disposal that has proven to be capable of simulating volcanic ash dispersion. The model is currently extended to also simulate dust mobilization and the subsequent dust transport and deposition. FLEXPART can deliver spatio-temporally resolved size-resolved dust deposition fields, which can be used directly to compare with observations of albedo and/or run-off.

Figure 1. (a) The eruption plume from the Eyjafjallajökull volcano, and some resuspended ash, at 13:15 LT on 17 April 2010. (b) Summary data for dust event on 28 April, 2007. MODIS Aqua image 13:45 (local time) showing dust blowing from Landeyjasandur and Markarfljót (on the coast just north of STO; Fig. 1) toward Reykjavik on April 28, 2007. (c) Wildfire at Mýrar on 30 Mars 2006, at 12:55. Images are courtesy of MODIS Rapid Response System at NASA/GSFC.

Figure 2. Eyjafjalla- and Mýrdalsjökull 24 May 2010. (b) Langjökull, Hofsjökull and Vatnajökull (left to right) on 2 June 2010. Images are courtesy of MODIS Rapid Response System at NASA/GSFC.
CONCLUSIONS

The mass- and energy balance observations from 2010 on Langjökull and Vatnajökull were remarkably singular from the more climatically driven mass- and energy balance of the years 1992-2009. The tephra from the Eyjafjallajökull eruption highly reduced the albedo of Langjökull and Vatnajökull, and significantly magnified the melting within the accumulation areas where up to three years of accumulation was melted away. The specific balance was -2.8 m a\(^{-1}\) w.e. on Langjökull in 2010, or more than twofold the average loss of -1.3 m a\(^{-1}\) w.e. of the warm years 1996-2009. For Vatnajökull, the specific balance was -2.1 m a\(^{-1}\) w.e. in 2010, also more than two times the average loss of -0.8 m a\(^{-1}\) w.e. from 1996-2009.

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REFERENCES


ANALYSIS OF PARTICLE NUMBER SIZE DISTRIBUTION CHANGES BETWEEN THREE MEASUREMENT SITES IN NORTHERN SCANDINAVIA

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Keywords: AEROSOL DYNAMICS, AIR MASS ANALYSIS

INTRODUCTION

In the rural boreal forest areas up to half of the aerosol mass concentrations are estimated to originate by condensing from biogenic gaseous precursors emitted from the vegetation (Tunved et al., 2008). The climatic potential of these particles depends on the aerosol dynamical processes taking place during the atmospheric transport. Particularly, the condensational growth is important, since secondary particles need to reach diameters larger than about 50-100 nm in order to participate in cloud droplet activation (Kerminen et al., 2005).

METHODS

We analyzed the particle number size distribution evolution when air masses travel hundreds of kilometers, and also examined the new particle formation in three measurement sites at Northern Scandinavia. For this, we used the measured aerosol size distribution data together with the modeled air mass trajectory data.

Two of the measurement sites, Väärö SMEAR I station and Pallas GAW stations are situated in Finland and the last one, Abisko in Sweden near the border of Norway (Fig. 1). The sites are located roughly along a straight line from west to east on latitudes 67-68 °N. The distance from Abisko to Väärö is 440 km. The area surrounding Abisko is dominated by subarctic mires, birch forest, and mountain tundra. The Scandinavian mountains are west from the station and after them is the coast of the Atlantic Ocean at c. 100 km from the station. Pallas and Väärö are surrounded by boreal forest. The Pallas station itself is situated above the tree line.

Our aerosol number size distribution data were collected between August 2005 and December 2007. The data was measured using Differential Mobility Particle Sizers (DMPS) with cutoff sizes of 3 and 7 nm in Väärö and Pallas, respectively, and using a Scanning Mobility Particle Sizer (SMPS) with a cutoff size of 10 nm in Abisko. The measurements at Pallas and Väärö are continuous, whereas the Abisko data were collected during campaigns of several months and covered c. half of the days during the analyzed period. We analyzed and compared the new particle formation events from each site according to the scheme created by Dal Maso et al. (2005). The days were classified as events, non-events and undefined days. For
the event days we fitted the particle number size distribution data to sum up to three lognormal distributions, and calculated the growth and formation rates of the nucleating particles.

Figure 1. A map of Northern Scandinavia. The measurement stations are located approximately in line from west to east in the following order: Abisko, Pallas, Värrö (A, P, and V in the map). (Map: Natural Earth data)

Tunved et al. (2006) had shown that the aerosol mass loading was linearly proportional to the time the air masses had been over continent after arriving from ocean. Here we repeated and broadened their analysis to cover also Abisko, and compared the growth of particles as a function of time the corresponding airmass had spend over land separately for all three measurement station. The HYSPLIT trajectory model (Draxler and Hess, 1998) was used to calculate the over-land times. Particle size distribution data from several measurement stations combined with the calculated airmass trajectory information allowed us to study regionally the dynamical changes of aerosol particle populations. For this, we concentrated on the air masses that passed two measurement stations. For each these station pairs, we compared the aerosol size distributions between the upwind and the downwind station. When studying the aerosol dynamics, the initial states need to be comparable. For this, we clustered the particle size distributions measured at the upwind station to obtain a set of initial states. We calculated the mean, 16th and 83th percentiles of the corresponding size distributions, as well as fitted a sum of lognormal distributions to the mean size distributions at both ends of the path.

RESULTS AND CONCLUSIONS

Our results (Väänänen et al., 2013) from the new particle event analysis showed that during nucleation the mean particle growth rates for the three stations varied between 2.8 and 3.7 nm/h (highest in Abisko) and the mean formation rates for the stations were between 0.09-0.1 cm$^{-3}$s$^{-1}$. This was in line with previous studies (e.g. Dal Maso et al., 2008).

When the average properties of aerosol population in the growing season were studied, the particle mode diameter, the accumulated mass concentration and the condensation sink were found to have linear increasing apparent trend as a function of time the corresponding airmass had spent over the continent after arriving from the ocean. These increase rates were calculated and they had values close to each other between the measurement stations. The similarities between the stations were probable linked with the general characteristics of the biogenic emissions from the boreal forest zone. The apparent growth rates of the particle diameters varied between 0.5-0.7 nm/h, and were several times smaller than the average growth rates during the evident new particle formation events. The apparent growth did not change significantly when only days without new particle formation were considered. The linear accumulation of the particle diameter, mass concentration and condensational sink were observed to occur at least 96 hours, whereas the particle concentration grew up to until 30-40 hours and after that saturated towards values of order of 1000 cm$^{-3}$.  

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Figure 2. The dynamics of particle size distributions when air masses are moving from one measurement site to another. Summer season 1.4.–30.9. covered. The initial size distributions at the upwind station are clustered to obtain as similar initial states as possible. Each subplot represents one cluster. The first one of the site pair is the upwind site, and the second one is the downwind site. The cluster mean size distribution at the upwind station is plotted with solid red line, and the shadowed red area shows the percentiles between 16 and 83. Similarly, blue solid line is the mean of the corresponding size distributions at the downwind station, and shadowed blue area shows the above mentioned percentiles. The number $n$ shows the amount of size distribution pairs in each cluster.

When studying the air masses that were travelling from one measurement site to another, the wind direction was found to have a clear effect on the dynamics of the aerosol size distributions. For each measurement site-pair, the size distributions at the upwind station were divided to 3-5 clusters and the dynamics of each cluster were analyzed. When the air masses originated mainly from the ocean and travelled from west to east, the concentrations of the Aitken particles of the most dominated clusters were
found to increase with rates of 0.01-0.02 cm$^{-3}$s$^{-1}$ during the transport and the mode peak diameters of them shifted towards larger particles with rates of 0.6-1.2 nm/h. This average shift of the particle diameters had an increase rate close to the apparent growth rate obtained when analyzing the aerosol dynamics over the continent. For the opposite wind direction the air masses originated from the continent and much slighter changes on the size and concentration of the Aitken mode particles were seen. Our results indicate that the condensational growth plays a role also when no evident nucleation is observed.

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REFERENCES


Aerosol emission reductions over the 20th and 21st century and their impact on polar climate.

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Keywords: AEROSOL, EMISSIONS, ARCTIC, EUROPE, CLIMATE.

INTRODUCTION

Large changes in the magnitude and spatial patterns of global aerosol emissions have occurred during the 20th century and are projected to continue over the coming century. Of particular relevance for the Arctic are the reductions in sulfate emissions from industrial activities, domestic heating, and power production that have taken place in Europe during the latest decades. These changes provide an opportunity to study in detail how regional emissions over Europe affect the radiative balance and the global and Arctic climate. Detailed estimates of the European emission reductions are readily available, in addition to temperature and radiation measurements.

METHODS

Transient climate simulations over the industrial period (1850 to present) from the Norwegian Earth system model NorESM (Kirkevåg et al., 2013) with different emission levels will be conducted and analysed. The simulated aerosol number size distribution and mass composition will be evaluated versus in-situ observations from different European measurement networks. The analysis will then be focused on Europe and the European sector of the Arctic and how surface radiative flux and temperature changes relate to different emission scenarios. As a first step, we will present results from a comparison between the “best guess” 1850 to 2005 NorESM simulations with simulations using constant 1850 SOx emissions globally.

CONCLUSIONS

It is not clear how the Arctic climate is affected by changes in global and European aerosol emissions. As more and more countries adapt different strategies to reduce air pollution, it is important to examine how this will affect not only the top-of-the-atmosphere radiative forcing, but also the surface temperature and other parameters important for society. The project presented here is aimed at shedding light on this particular problem.

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REFERENCES
SERIES OF EXPERIMENTS ON THE EFFECTS OF SOOT ON SNOW

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Keywords: BLACK CARBON, SNOW, ALBEDO

INTRODUCTION

Soot particles contain black carbon (BC) and organics. When soot particles get deposited on snow the BC and also some of the organics will absorb solar radiation. This leads to a decrease of the snowpack albedo, heating of the snow and acceleration of its melting (e.g., Warren and Wiscombe, 1980; Clarke and Noone, 1985; Flanner et al., 2007; Quinn et al., 2008). These effects may be responsible for as much as a quarter of the observed global warming (Hansen and Nazarenko, 2004).

The above-mentioned effects have been investigated in the Soot-on-Snow project. It consists of a series of experiments aimed for studying the effects of soot on snow, for example the effect on albedo, snow grain size, and melting. Experiments have so far been conducted during three consequent late winters / springs. The first one of the series was conducted in spring 2011, the second in winter/spring 2012 and the latest one in spring 2013 (e.g., Meinander et al., 2013). The experiments were organized by the Finnish Meteorological Institute in cooperation with University of Helsinki Physics department, Finnish Geodetic Institute, and Agricultural University of Iceland.

METHODS

In all experiments soot was deposited on snow but with different methods. In the first campaign in 2011 soot particles were produced by burning various organic materials in a wood-burning stove. The smoke was lead through a pipe, cooled by snow surrounding the pipe, and lead into a rectangular chamber on top of the snow. In 2012 the soot was first acquired from a chimney-sweeping company in Helsinki. The chimneys the company had cleaned were in residential buildings with small-scale wood burning. The soot was blown into a cylindrical (diameter 4 m) chamber laying on snow of a farming field.

The blowing system consisted of a blower, a tube blowing air into a barrel filled with the soot, and a cyclone that removed largest particles. In 2013 the blowing system was modified so that the amount of soot blown could be controlled. The soot was from the same source as in the 2012 experiment, i.e., from small-scale wood-burning chimneys but also from chimneys from buildings with an oil burner and from a peat-burning power plant.

In addition, in the 2013 experiment, Icelandic volcanic sand and glaciogenic silt were blown over the snow. The volcanic sand was a near black mixture of the volcanic ash of glaciofluvial nature, originating from under the Myrdalsjokull glacier, which may be mixed with the ash of the Eyjafjallajokull eruption in 2010 and the Grimsvotn eruption in 2011. The glaciogenic silt was lighter in colour than sand, from light-brown to slightly yellowish colour consisting mainly of silt and some coarse clay sized particles, capable
of being transported and deposited on the local glaciers as well as several hundreds of kilometres towards the Europe (Arnalds et al., 2013).

After depositing the soot, pyranometers were set up over the soot and reference fields to measure incoming global radiation and reflected radiation. From the ratio the albedo was calculated. Snow samples were taken and analyzed for elemental and organic carbon with a Sunset Labs EC/OC analyzer. Snowpack thickness was measured, and a physical characterization of snow stratigraphy was done, including thickness, density, hardness, grain size and shape, and temperature. In addition, the spectral reflected and transmitted irradiance was measured for some spots.

The first experiment was conducted at a private farming field in Nurmijärvi, southern Finland in March – April 2011. The second experiment was conducted at the FMI observatory in Jokioinen, southern Finland in February – March 2012. The third experiment was conducted at the Sodankylä airfield near the FMI Sodankylä observatory, Finnish Lapland in April – May 2013.

RESULTS AND DISCUSSION

The experiment demonstrated very clearly the effects of soot on snow: the albedo decreased, the snow grain size, the whole stratigraphy, temperature profile, and melting rate in the snow pack changed compared with the reference site. The albedo of the snowpack decreased logarithmically as a function of elemental carbon concentrations (Figure 1). The data are in a fairly good agreement with the laboratory experiments and modeled data of Hadley and Kirchstetter (2012).

![Figure 1. Albedo of snow at solar noon as a function of Elemental Carbon concentration in snow.](image)

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AGEING SOOT AS CLOUD CONDENSATION NUCLEI

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Keywords: CCN, AMS, Black Carbon, Organic compounds.

INTRODUCTION

Soot particles are commonly occurring in atmospheric aerosol, especially in urban areas. Freshly emitted soot particles, often referred to as black carbon (BC), are known to have a predominantly warming effect on the climate (IPCC, 2007). The ability of BC to absorb light is referred to as a direct aerosol effect on our climate. However, BC is also considered to have an effect on Earth hydrological cycle, i.e. an indirect effect on the climate. But the knowledge is sparse regarding interactions between clouds and BC co-emitted with organic carbon (OC). The lack of knowledge causes large uncertainties in net climate forcing estimates (Bond et al., 2013). Part of the oxidation products from intermediate-volatility organic compounds (IVOC) or volatile organic compounds (VOC), co-emitted or already appearing in the atmosphere, may condense or coagulate onto the BC particles and form secondary organic aerosol (SOA). SOA formation processes will increase the possibility of BC particles to better become cloud condensation nuclei (CCN). In this study the change in cloud activation properties of BC particles exposed to photo-oxidized anthropogenic precursors (in the diesel exhaust as well as additives of toluene and m-xylene) have been experimentally investigated.

METHODS

Diesel exhaust from a Euro 2 passenger vehicle (DEP experiments) and exhaust from a flame soot generator (FSP experiments) was transferred into a smog chamber and photo-chemically aged (Nordin et al., 2013). VOCs and IVOCs in the diesel exhaust were used as SOA precursors as well as toluene and m-xylene were added to allow investigations of the full particle transformation from agglomerates to spheres. The aerosol properties were monitored with regard to morphology, density, volatility, particulate and gas composition, and cloud droplet nucleation. The point of activation into cloud droplets was related to the organic fraction in the particle as well as particle size and morphology throughout the ageing process.

Cloud-activation properties were measured with respect to critical supersaturation (SS) using a Cloud Condensation Nucleus Counter (CCNC; DMT 100). A soot particle aerosol mass spectrometer (SP-AMS, Aerodyne research) was used to determine the composition of the cores and the coatings of the particles. The particle mass-mobility relationship was characterized using a Differential Mobility Analyser-Aerosol Particle Mass Analyzer (DMA-APM; Kanomax Japan 3600; McMurry et al., 2002). A thermodenuder was introduced in series between the DMA and the APM, used for quantification of the size dependent mass fraction condensed onto the non-volatile soot cores. The particles were first size selected by a DMA, according to their mobility diameter (d_m), followed by measurements in the APM and CCNC. The CCNC was operating in two different modes. Firstly, it ran in the traditional way of changing the supersaturation (SS) step-wise. Secondly, the CCNC operated in Scanning Flow CCN Analysis (SFCA) (Moore and Nenes, 2009), enabling rapid measurements with high time resolution of the supersaturation spectra by scanning the airflow in the instrument.
CONCLUSIONS

Results show time-dependent changes of activation properties of the organic coated soot cores as well as changes in morphology to a more spherical-like shape (Fig.1). Freshly emitted soot particles does not activate as CCN. At the onset of UV exposure the first activation of the exhaust particles is seen, followed by a decrease of the critical supersaturation (Fig.1, blue). The decrease in $SS_c$ can be attributed to four factors: (I) SOA mass fraction ($SOA_{mf}$) of the particle, which is increasing throughout the experiments (Fig.1, green); (II) type of organic coating, e.g. in the beginning the O:C≈0.1 for the diesel exhaust particles, corresponding to urban atmospheric aerosol, and requires a higher $SS_c$ than in the end, when the O:C≈0.45, typical for an aged atmospheric aerosol; (III) particle size, e.g. a size-dependency with lower $SS_c$ for larger selected mobility diameters ($d_m$) (Fig.2, colour coding); and (IV) morphology, e.g. the volume equivalent diameter ($d_{ve}$) changes throughout the experiments (Fig.2). These results indicate that the ageing of soot particles do affect the cloud forming properties of the particles to such a degree that they can actually become CCN in the atmosphere.

Figure 1. At the onset of UV exposure a drastic decrease in $SS_c$ is seen (blue), as well as an increase in SOA mass fraction ($SOA_{mf}$, green) and volume equivalent diameter ($d_{ve}$, black). Results for aged diesel exhaust particles (DEP) with a mobility diameter ($d_m$) of 150 nm.

Figure 2. Measured values of the $SS_c$ for different volume equivalent diameters ($d_{ve}$), size-selected according to their mobility diameter ($d_m$, colour coded; 60 nm FSP, dark blue; 90 nm FSP, light blue; 150 nm FSP, turquoise; 150nm DEP, green; 300 nm FSP, orange). Results from soot generator (FSP 1 and 2, circles and diamonds, respectively) and diesel exhaust (DEP, triangles) experiments. Lines are modelled results for different $\kappa$-values, where $\kappa_{wettable}=0$ (black) corresponds to activation of a wettable but insoluble particle and $\kappa_{AS}=0.56$ (lightest grey) corresponds to activation of an ammonium sulphate particle. $\kappa_{SOA}=0.13$ is the calculated value for the SOA appearing in the end of the experiment.
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Surfaces for Water harvesting
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Keywords: Dew, Fog, Water-harvesting.

systems by investigating the usability of dew collectors as harvesters of water vapor directly from the atmosphere under (semi-)arid climate conditions.

INTRODUCTION

Availability of water is one of the most severe developmental challenges of the world. Water scarcity already affects every continent and more than 40\% of the people on the Earth. By 2025, approximately 1.8 billion people will be living in countries or regions with absolute water scarcity, and two thirds of the world’s population could be living under water stressed conditions (FAO, 2007). In this project, the aim is to provide practical solutions to water shortages in developing countries in arid and semi-arid environments, by investigating the usability of dew collectors as harvesters of water vapor directly from the atmosphere under (semi-)arid climate conditions. The hypothesis is that utilizing cost-effective and environmentally safe modern materials as a substrate to collect dew will initiate development and production of dew collectors not only among Finnish industry but also among local industry in the developing countries.

METHODS and MATERIALS

According to Nilsson et al., (1994) a ”dew collector material should display a high emittance (or equivalently a high absorption) in the infrared wavelength range, in order to experience a high thermal power loss leading to a low temperature at the surface. In addition the solar reflectance should be high in order to collect dew for some period after sunrise and to prevent evaporation of the collected water from the surface.” Following these design specifications, dew will condensate on such a surface if the temperature sinks below the dew point of the surrounding air mass. The key advantage of such an approach is the passive nature of the collector, which relies only on the creation of a local temperature gradient through emission spectrum bands of included pigments.

Surface matrix

For the surface matrix two possible polymers will be tested. The first one is polyethylene (PE), which is a thermoplastic polymer consisting of long hydrocarbon chains. PE is the cheapest polymer and has excellent chemical resistance, meaning that it is not attacked by strong acids or strong bases. It is also resistant to gentle oxidants and reducing agents in the atmosphere.

The second polymer is polylactide (PLA), which is a thermoplastic aliphatic polyester derived from renewable resources, such as corn starch, tapioca roots, or sugarcane. In addition to the origin from renewable resources the material is also biodegradable.
Pigments
For the embedded pigments in the surface matrix we have decided on four compounds which alone or on combination with each other have a high solar reflectance in the UV/Vis and a high absorption in the IR (wavelengths 8-13 um).

\textit{ZnS}
Zinc sulfide is an inorganic compound with the chemical formula of ZnS. Zinc sulfide is a good infrared optical material, transmitting from visible wavelengths to just over 12 micrometers (Cotton, Wilkinson and Gaus, 1995).

\textit{CaCO\textsubscript{3}}
Calcium carbonate is a chemical compound with the formula CaCO\textsubscript{3}. Calcium Carbonate has several absorption peaks in the atmospheric window and has the additional advantage of being very cheap (Cotton, Wilkinson and Gaus, 1995).

\textit{BaSO\textsubscript{4}}
Barium sulfate is an inorganic compound with the chemical formula BaSO4. In addition to its high reflectance in the UV/Vis it is used as polymer filler due to its effect of increasing acid and alkali resistance and opacity (Cotton, Wilkinson and Gaus, 1995).

\textit{TiO\textsubscript{2}}
Titanium dioxide, is the naturally occurring oxide of titanium, chemical formula is TiO2. Titanium dioxide is known for its brightness and very high refractive index. Used as a pigment it provides whiteness and opacity (Cotton, Wilkinson and Gaus, 1995).

OUTLOOK
With the above mentioned parameters, we intend to design polymer foils which are able to harvest water vapour from the atmosphere. The foils will be tested and evaluated in the lab on their performances. A device which mimics the night sky is used to determine the radiative cooling power of each foil. The amount of condensed water vapour is determined using gravimetry.

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REFERENCES


MODELING THE IMPACT OF CLIMATE CHANGE ON OZONE AND PM$_{2.5}$ CONCENTRATIONS IN THE ARCTIC

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INTRODUCTION

Recently, there has been a growing interest in the effects of climate change on the future air pollution levels (Hedegaard et al., 2012; 2013). Since the industrialization the concentration of greenhouse gases in the atmosphere has increased. According to the IPCC report (2007) some meteorological parameters will also change in the future due to the man-made changes of the composition. On the other hand, nearly all processes influencing the atmospheric composition such as atmospheric transport, chemical reactions and photolysis rates, wet and dry deposition levels and emissions are directly determined by the different weather parameters. Therefore it is hypothesized that a changed future climate will have an impact on future levels and distribution of air pollution concentrations in the atmosphere.

METHODS

This specific hypothesis is tested using a one-way coupled climate-chemical transport model system setup. The hemispheric chemical long-range transport model DEHM (Danish Eulerian Hemispheric Model; Brandt et al., 2012) is used in the current experiment to investigate the future air pollution levels in the Northern Hemisphere with special emphasis on the Arctic. The coupled atmosphere-ocean model ECHAM5/MPI-OM provides 21st century meteorology and part of the 20th century based on the IPCC SRES A1B scenario every 6 h as input to DEHM. In order to save computing time the experiment is focused on two decades instead of simulating the 21st century in one continuous run. The periods are 1990–1999 and 2090–2099. These time-slices are simulated with constant 2000 anthropogenic emissions in order to separate out the effects on air pollution from climate change. However, since this work focus on estimation of the size and sign of the impact from changes in climate on ozone and fine particles, the biogenic emissions of volatile organic compounds (VOC) are allowed to vary. Isoprene is the most abundant biogenic VOCs and is an important species for the ozone formation. Furthermore, monoterpenes formed by isomers of two isoprene units and as well as isoprene can contribute to production of organic particles. Recently, Zare et al. (2012, 2013) described an updated version of DEHM including online estimation of the biogenic VOCs of isoprene and monoterpenes emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature; Guenther et al., 2006).

CONCLUSIONS

Preliminary results show significant changes of the future levels of ozone and PM$_{2.5}$ concentrations in the Arctic due to future climate change. More and detailed results from the simulations will be presented at the meeting.

REFERENCES


