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Editors: Markku Kulmala, Jaana Bäck, Magdalena Brus and Tuomo Nieminen

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Background and summary

Climate change is proceeding fastest at the Arctic, its near-surface warming being about twice the global average during the recent decades. Simultaneously, the Arctic cryosphere has experienced notable changes: the sea-ice area has been decreasing, and precipitation and river discharges into the Arctic Ocean have been increasing. The changes have dramatic impacts on the Arctic ecology and societies.

There is no consensus on the reasons why climate changes so fast in the Arctic, and whether the amplified warming will continue. It is clear, however, that the Arctic surface radiation balance regulates the melting and freezing of the pack ice, a key climate regulator. Simulations of Arctic clouds are particularly deficient, impeding correctly simulated radiative fluxes. Important, yet poorly-quantified players in this context are short-lived climate forcers (SLCF): natural and anthropogenic aerosols, ozone and methane.

The climate impacts of SLCFs are tightly connected with cryospheric changes and associated human activities. Transport of black carbon aerosols into high latitudes and their deposition on snow decrease the surface albedo. Together with decreased sulfate aerosol emissions it has probably contributed to the observed Arctic warming. Melting of the pack ice and sea ice is likely to result in increased numbers of aerosol particles and CCN from sources in the high Arctic, which increase the reflectivity of clouds. Properties of high-latitude clouds may also be affected by the changing biogenic aerosol formation associated with warming and snow-cover changes over boreal forest regions. Emissions of methane from thawing permafrost and coupling of atmospheric methane oxidation with ozone formation affect Arctic greenhouse gas forcing. Finally, cryospheric changes alter human activities in Arctic and Nordic regions, which changes anthropogenic emissions of SLCFs over these areas.

The on-going Arctic climate change and cryosphere are interlinked via the following five components (Fig. 1): A) Radiative forcing, B) Arctic warming, C) Changes in the cryosphere, D) Society and human activities, E) Feedbacks in the climate system. Traditionally, the enhanced warming of Arctic areas, as compared with the Earth as a whole, has been explained by the so-called ice-albedo feedback (IPCC, AR4 2007), which involves the loop A -> B -> C -> A (loop 1).
Here, we will expand the above thinking to include the roles of society and associated human activities (component D), as well as feedbacks other than the traditional ice-albedo feedback (component E). Related to the component D, two potential feedback loops with different starting points can be identified. First, future reductions in ice and snow cover affect human activities and concomitant emissions in the North through changes in cargo ship traffic, travel and tourism industry, oil exploration and production, fishing and agriculture. This can be described with the loop C -> D -> A -> B -> C (loop 2). Second, the society has a potential to influence Arctic warming via either targeted emission control actions or geoengineering, both corresponding to the loop D -> A -> B -> (C) -> D (loop 3). The Arctic climate system itself involves a number of yet poorly-understood feedback processes initiated by changes in i) the heat balance over surface, ii) moisture budget, or iii) natural emissions of aerosols and their precursors, and formation of secondary aerosols including also ozone which is a potent greenhouse gas (IPCC, 2007, Quinn et al. 2008). Collectively, these feedbacks can be described with the loop A -> B -> (C) -> E -> A (loop 4).

Our main aim is to quantify the feedback loops 1-4, and especially to address how the loops 2-4 compare with the loop 1 in their potential magnitude. We will focus our attention on the role played by short-lived pollutants (recently also called short-lived climate forcers, SLFC) and clouds and their linkages with cryospheric changes because i) their role in Arctic warming is potentially very large, yet poorly quantified, ii) their emissions are expected to be changed considerably as a result of future warming and associated changes in human activities, and iii) they might provide an additional mitigations pathways for future Arctic warming.
Objectives to be achieved

Our general objectives are i) to identify and quantify the major processes controlling Arctic warming and related feedback mechanisms, ii) to outline strategies to mitigate Arctic warming, and iii) to develop Nordic Earth System modeling. More specifically, we aim to clarify:

**General scientific understanding of the Arctic climate system:**
- What are the main reasons for the amplification of Arctic warming
- Why is warming more pronounced in winter
- What are the relevant feedbacks
- What can we learn from past and recent changes in Arctic climate

**Specific questions related to cryosphere:**
- How is albedo changing over sea and land surfaces
- How is radiative forcing changing at the surface and top-of-the troposphere, and which forcing agents and feedback factors are responsible for it
- How do cryospheric changes affect natural emissions and surface heat exchange
- How do emissions of halogen compounds and other key species from snow and sea ice respond to changing loads of pollutants
- How do Arctic clouds respond to emissions and changing climate
- How are the magnitude, phase and spatial pattern of precipitation changing
- What is the relative role of anthropogenic and natural aerosols
- How important is BC on snow/ice in the Arctic radiative balance
- How do all the above issues vary seasonally and regionally
- How is the variability in seasonal snow and ice extent determined

**Mitigation issues:**
- How effective would different emission control strategies be using short-lived pollutants to mitigate Arctic warming and melting sea ice
- What is the best way to control emissions if both climate change and air pollution issues are considered
- Do we need to consider the feedback loop 2 when designing mitigation strategies
- How does increasing human activity in the Arctic affect the Arctic climate
- Does geoengineering provide an option for mitigating Arctic warming

**Nordic climate and Earth System modeling (ESM):**
- How has the atmospheric composition and the associated radiative forcing changed during the past 10000 years and how will they change during the next 150 years
- How can we obtain reasonable and relevant information on what could occur if the Arctic was 5 K warmer than today
- What is the best way to implement the current process level understanding to improve ESMs and their parameterizations
- Which Earth System model components are the most important to develop further
- Integration of cryosphere component models into ESMs

**Methods**

In order to be able to meet our objectives, and to answer our research questions, we need to perform multi-scale and inter-, multi- and cross-disciplinary research with a high level of
technological and scientific innovation. Our approach relies on existing Nordic research infrastructures and various measurement and modeling tools.

The scientific work will be divided into 8 Work Packages in different thematic areas

WP1: Coordination, knowledge transfer and dissemination
WP2: Cryospheric changes
WP3: Natural emissions associated with warming and cryospheric changes
WP4: SLFC and cryosphere
WP5: Cryosphere-aerosol-cloud-climate interactions
WP6: Atmosphere-cryosphere-societal interactions
WP7: Past long-term changes in the Arctic
WP8: Synthesis, Integration and Earth System

The main research tools to be exploited are the following:

**In-situ field observations**
Field observations will be made on ground-based stations, air craft and ships, in addition to using existing data sets and archives. Data on short-lived pollutant concentrations in air, on snow and ice surfaces, seasonal evolution of terrestrial and oceanic snow and ice cover, surface radiation and heat exchange, fluxes of key species, cloud properties and relevant meteorological data are obtained. The observation network consists of existing intensive stations and their measurement programs (snow, inland waters, permafrost, basic aerosol microphysics, optics, and chemistry), including quality analysis (QA) and data dissemination procedures developed in other projects. These are outfitted with additional instruments addressing the research questions. To ensure long-term sustainability and comparability, these measurements are connected to international networks wherever possible.

**Remote sensing by satellites**
Satellites will be used to retrieve information on e.g. aerosol and cloud properties, snow cover, ice extent, surface albedo, top of atmosphere radiation and BrO data. Many of the relevant quantities are measurable only from satellites. Satellites complement in-situ and modeling data related to chemistry (e.g. BrO and other trace gases), aerosols, clouds and their interactions, especially for the spatial and temporal distribution pattern of relevant quantities. Derived data are used to evaluate large-scale models simulating important Earth System components.

**Laboratory experiments and field campaigns**
The long-term monitoring network will be complemented with target-oriented field campaigns and lab experiments. Specific campaigns include annual UAV (unmanned aerial vehicle) campaigns, cruise expeditions on research ships, dedicated mountain top (in-cloud) field campaigns, winter-season evolution of snow and ice in selected drainage basins, snow and ice-related ecological studies and airborne studies.

Lab experiments focus on ice nucleating properties of various natural and anthropogenic aerosols and their mixtures, and snow and ice processes. The understanding of how cold and mixed-phase clouds interact with changing Arctic pollutant concentrations and climatic conditions is essential.

**Ice core data**
Past variations in climate and SLFC are revealed by analysis of firn and ice cores in glaciers and ice sheets. In a first step it is necessary to distinguish between different sources to be able to make predictions about which sources have dominated emissions during different climates and
environmental conditions. The sulphur isotope ratio in snow and ice samples can be used as a tracer for different aerosol sources during different climatic conditions. Many firn and ice cores from Greenland ice sheet, in ice caps in the Canadian Arctic and in glaciers on Svalbard have been analyzed for their content of impurities beside climate information and physical properties. The resolution of the records depends on the snow accumulation rate at the drill site and the sample preparation and analytical technique. Our data from Greenland (GRIP, NGRIP and NEEM) reveal that the northern hemisphere polar atmospheric circulation can totally change mode from one year to the next at very abrupt climate change from cold stadials to warm interstadials/interglacials. Current climate models lack the ability to generate changes this rapidly.

**Modeling**

Process models are used to identify the importance of different processes on short-to-moderate temporal and spatial scales, to extrapolate measurement results and to predict future scenarios. The models, like observations, cover various spatial and temporal scales and are implemented in a hierarchical structure. The models applied by the consortium range from detailed process models (e.g. UHMA, SALSA, CALM, ADCHEM) up to regional and global chemical transport and climate models (e.g. EMEP, MATCH, DEHM, ECHAM, OsloCTM2, UCLA LES, WRF-CHEM, CAM-Oslo), radiative transfer models (DISORT), and to Earth System models (e.g. COSMOS, NorESM, EC-Earth).

The field stations involved are:

1. Troll station, Antarctica
2. Vavilhill, S-Sweden
3. Birkenes, S-Norway
4. Lille Valby, Denmark
5. Vindeby, Denmark
6. Sørø, Denmark
7. Aspvreten, central Sweden
8. SMEAR III, S-Finland
9. SMEAR II, central Finland
10. SMEAR IV, Kuopio, central Finland
11. Sodankylä, N-Finland
12. SMEAR I, Värriö, N-Finland
13. Abisko, N-Sweden
14. Pallas GAW station, N-Finland
15. Tiksi, Siberia
16. Daneborg and Zackenberg, Greenland
17. Ny-Ålesund, Spitzbergen
18. Station Nord, Greenland
RESULTS FROM THE FIRST YEAR

During the first year the CRAICC community has initiated several research themes, which will be further developed in the rest of the funding period. The WWW-pages were opened in http://www.atm.helsinki.fi/craicc/ and these pages are used for distributing information e.g. of open fellowships and upcoming events.

A kick-off meeting was arranged in Helsinki in the beginning of February, 2011. In the kick-off the WP leaders presented the plans for contents of each WP, and group discussions about activities in each theme were also included in the program. Other activities have included:

1. Fellowships
   The two fellowship calls in 2011 yielded 16 fellowship proposals, where two or more partners jointly planned a joint post-doc or doctoral project. The accepted fellowships (by Oct 1st) were ‘Sources, fate and transport of SLCFs’, ‘Long-term reconstructions of the arctic tree-line’, ‘Absorbing aerosol deposition on snow and its climate effects’, ‘Emission inventories of biogenic emissions of VOC from vegetation in Siberia and North America’, ‘Quantifying inland water CO$_2$ emissions with decreasing ice cover duration’, ‘Sea spray sources at low temperatures’ and ‘Linking Svalbard ice core records to atmospheric measurements at Zeppelin station’. The first fellowships were filled in the summer 2011.
2. Networking
Two Ice Nucleation Workshops were organized, the first one in spring in Copenhagen and the second one in fall in Helsinki. The talks in Copenhagen represented different aspects of ice nucleation: including theoretical and experimental studies on molecular level, laboratory studies on aerosols and ice, instrument development, as well as global modelling of the importance of ice nucleation. The Helsinki Workshop presentations outlined the basic concepts and theoretical framework of 1) homogeneous gas-to-liquid and liquid-to-ice nucleation 2) heterogeneous gas-to-liquid, liquid-to-solid and gas-to-solid nucleation. Concepts and main features of different types of homogeneous and heterogeneous nucleation were compared to each other. The stochastic and singular hypotheses in ice nucleation were explained, and a classical nucleation theory based modeling approach was presented to explain the apparently singular behavior based on underlying stochastic processes.

Several short visits (3-14 days) were arranged by the CRAICC partners, for planning future activities and to create joint initiatives (e.g. fellowships).

3. Education
An intensive field course for the Finnish participants of CRAICC from the University of Helsinki was held in August 2011 in Kilpisjärvi, Finnish Lapland. The objective was to introduce the participants on special features of the Arctic and the cryosphere-atmosphere interactions. The attendees presented basics of their research fields and insights to their own research especially in relation to the Arctic. Discussed themes were northern ecosystems (forests, wetlands, tundra, lakes and the Arctic Ocean); biogeochemical cycles in the North; processes of the Arctic Ocean, periglacial and glaciers; Arctic climate change and northern atmospheric processes and air pollutants.

4. Other activities
The CRAICC partners were actively presenting their research results in several Cryosphere-related international meetings. These included e.g. the Committee on River Ice Processes and the Environment (CRIPE) conference (Manitoba), the 3rd iLEAPS Science Conference (Garmisch-Partenkirchen), Bert Bolin Climate Center annual meeting (Stockholm), American Geophysical Union (San Francisco), AMAP: The Arctic as a Messenger for Global Processes – Climate change and Pollution (Copenhagen), and the European Aerosol Conference (Manchester).
SNOWPACK CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS IN A BOREAL FOREST

H. AALTONEN¹, J. PUMPANEN², H. HAKOLA¹, T. VESALA³ and J. BÄCK²,³

¹Finnish Meteorological Institute, Finland
²Department of Forest Sciences, University of Helsinki, Finland
³Department of Physics, University of Helsinki, Finland

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INTRODUCTION

Emissions of the volatile organic compounds (VOCs) in the boreal forest at the branch and canopy levels have been rather well characterised (Hakola et al., 2003; Hakola et al., 2006; Ruuskanen et al., 2005), in contrast to the soil VOC exchange. Also wintertime above canopy VOC concentrations and fluxes from the canopy (Hakola et al., 2003; Hakola et al., 2009, Lappalainen et al., 2009) are known better than those from soil, which are practically unstudied. As the soil surface is covered by snow a substantial part of the year in the boreal zone, we conducted terpenoid concentration measurements inside the snowpack. So far have been published just a few studies reporting measurements of snowpack gas concentrations (e.g. Helmig et al., 2009; Kos and Ariya, 2010), and those studies have been concentrated mainly on other VOCs than terpenoids.

During the growing season, the above- and below-ground parts of plants are likely a source of forest floor and soil VOCs, as well as the diverse and effective soil microbial populations maintained by the forest ecosystem (Janson, 1993; Hayward et al., 2001; Asensio et al., 2008; Leff and Fierer, 2008; Bäck et al., 2010). In winter, as a season of low activity for plants, these biological processes contributing to fluxes of volatiles are changing. Compounds from storages of fallen needles and other litter may be released during winter by decomposition and physical degradation. Due freezing and thawing cycles, the importance of physical breakdown/degradation of litter is in higher level during winter than other seasons of year. Also lower temperatures in litter and humus layers as well as missing root exudates may lower the activity of decomposing soil animals and microbes in winter. In addition to VOC sources in the soil, also microbes living inside and on the snowpack may produce VOCs, but also act as sinks for them (Helmig et al., 2009).

We measured the VOC, more specifically terpenoid, concentrations inside the snowpack in a boreal forest during two subsequent winters. With these measurements, we want to improve the estimate of the importance of winter season to annual VOC emissions in a boreal forest ecosystem.

METHODS

We measured snow pack VOC concentrations from a Scots pine forest at the SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations II) station (61°51’N, 24°17’E, 180 m a.s.l.), located in the vicinity of the Hyytiälä Forestry Field Station in southern Finland (Hari and Kulmala, 2005). The forest stand at the SMEAR II station is 46 years old and dominated by Scots pine (> 60% of the trees). The soil above the homogeneous bedrock is Haplic podzol on glacial till, with average depths of 0.5–0.7 m.

We performed the snow pack VOC profile measurements during winters 2008–2009 and 2009–2010, in periods when the soil was covered by at least 10 cm of snow. VOC concentrations were measured by three permanently installed profile collectors. A collector (Fig. 1) was constructed on three partly perforated circular polytetrafluoroethylene (PTFE) tubes, where the lowest tube was placed at the ground, the middle one at a height of 10–15 cm, and the uppermost 20 cm higher than the middle one. Samples
were collected by circulating air from the sampling tubes through Tenax-Carbopack-B adsorbent tube at a flow rate \( \sim 100 \text{ ml min}^{-1} \).

![Figure 1. Schematic figure of snow profile VOC collector. Grey areas represent perforated sectors.](image)

Samplings were performed app. once a month, each time consisting of four 15 min sampling periods, with 15 min gaps between them. While the tube content (\( \sim 0.2 \text{ L} \)) only would not have been enough for analysis, samplings prolonged to 60 min and were done in four periods to equilibrate the VOC concentrations between the sampling tubes and the snow around them. The samples were analysed in the laboratory, using a thermodesorption instrument (Perkin-Elmer TurboMatrix 650, Waltham, USA) attached to a gas-chromatograph (Perkin-Elmer Clarus 600, Waltham, USA) with a mass selective detector (Perkin-Elmer Clarus 600T, Waltham, USA). The detection limits varied from 0.04 to 0.60 ng per tube and the analytical error was \( \sim 6\% \), based on repeated analysis.

Snow depth was measured once in a week from seven points, starting from the first snow and ending after the completely melted snowpack. Snow water equivalent was measured in every second week from the same points with snow depth for estimating the diffusivity of the snowpack.

**RESULTS**

Temperatures of these two sampling winters differed greatly at the SMEAR II station (Fig. 2). In 2008–2009, temperatures were all the time higher than the 30-year average (Drebs et al., 2002), except for a cold period at the end of March. However, throughout the mid-winter 2009–2010 temperatures were notably lower than the average and continuously below zero for over three months, starting from the beginning of December. These two winters differed also regarding the amount of snow (Fig. 2). During the winter 2008–2009 the snow depth was throughout the winter clearly below the 30-year average (Drebs et al., 2002), while in the winter 2009–2010 it was very close to average. In the winter 2008–2009 the uppermost profiles were barely covered by snow only just the time of the thickest snowpack. The depth of snow in the winter 2009–2010 was app. twice of that in the previous winter, being \( \sim 60 \text{ cm} \) at maximum. Water equivalent of snow was as well two-fold in 2009–2010 compared to 2008–2009, representing \( \sim 10\% \) snow water density in both winters.
We detected 23 VOC compounds from the snowpack, 9 of them were monoterpenes and 7 sesquiterpenes. The most abundant VOC group was the monoterpenes, concentrations varying from 0.13 to 4.4 µg m\(^{-3}\) in the first winter and from 0.11 to 510 µg m\(^{-3}\) in the second winter. \(\Delta^3\)-carene and \(\alpha\)-pinene were the predominant compounds, followed by \(\beta\)-pinene, terpinolene, limonene and camphene. During the first winter, \(\alpha\)-pinene had the highest concentrations, but in the middle of the second winter, \(\Delta^3\)-carene became dominating. Sesquiterpene concentrations were generally less than half of the monoterpene concentrations (Fig. 3), maximum values being 1.6 and 2.4 µg m\(^{-3}\) in the first and in the second winter, respectively. Isoprene was detected in the first samplings in both winters, but its concentrations were negligible, reaching to 0.40 µg m\(^{-3}\) at the maximum.

During the first winter and the first two months of the second winter, mono- and sesquiterpene concentrations were clearly the highest at the ground level and decreased rapidly towards the snow surface (Fig. 3). During the last half of the second winter the order of profiles regarding to mono- and sesquiterpene concentrations changed in two out of three collectors. At the end of the second winter in those two collectors monoterpene concentrations, especially \(\beta\)-pinene, \(\Delta^3\)-carene and terpinolene, increased dramatically (up to 1700-fold). With other monoterpenes the increase varied from 10- to 200-fold and with sesquiterpenes the increase of concentrations was approximately 10-fold.

CONCLUSIONS

Snowpack in the boreal pine forest contains the substantial concentrations of terpenoids, especially monoterpens. In a virgin snowpack, concentrations decrease towards the snow surface, suggesting that the source was located either below ground or on the soil surface (litter). This was probably due to the active decomposition below the snow pack and supports the finding of Kähkönen et al. (2001) that decomposition process does not cease even slightly below zero temperatures.

The hard winter caused remarkable forest damages at the site during the measurement period, which is a likely reason for the dramatic increase in monoterpene concentrations at the end of the second measurement winter. The proportions of the concentrations of different monoterpens inside snowpack changed with the increased total concentrations, strengthening the assumption of a sudden change in VOC source, most obviously from ‘normal’ litter decomposition to damaged tree organs. Concomitantly with the increase in VOC concentrations, the highest concentrations were not anymore measured from the ground level, but instead in the middle or top profiles.

If we compare these snowpack VOC concentrations with our below ground measurements (unpublished), conducted during the snow free period, the magnitudes, excluding the exceptionally high concentration in the winter 2009–2010, are really equal. This emphasizes the significance of the snow cover period to soil/forest floor yearly VOC emissions and highlights the role of soil as a wintertime VOC source when other biological sources are less active.

The physical properties of snow may have the substantial effects of diffusion of volatiles in snowpack. The porosity of snowpack is one of the most important factors and with the depth of the snowpack easy to
measure. Vertical movements of gases might be blocked by ice layers, formed by freezing after periods of above zero temperatures. The second winter of our measurements was exceptional by totally lacking these kinds of warmer periods, thus snowpack being really homogenous. The ice layers inside snowpack may affect strongly on spatial gas fluxes by causing horizontal gas movements and then the release of gases into atmosphere through certain holes, like along tree trunks.

ACKNOWLEDGEMENTS

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REFERENCES


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INTRODUCTION

River and lake ice play an important role in the hydrology of northern watercourses. Ice does also have impacts on the use of rivers and lakes during winter time and on infrastructure build in or by the watercourses (Prowse et al. 2011). In Norway, hydropower is developed in numerous rivers over the entire country and today stands for 99% of the production of electrical energy. Ice formation and breakup may prove problems for the operation of hydropower plants in rivers, and particularly high head plants will influence the natural ice regime through releases of warmer water from reservoirs into the rivers. The scenarios for future temperature and precipitation may have significant impacts on the future ice regime (Beltaos and Prowse, 2009) by shortening the ice-covered season and also by providing a more unstable winter with more frequent break-ups. The project presented here has two purposes. One is to study how future climate scenarios influences ice formation in rivers and lakes on a larger (nationwide) scale; the second is to investigate how changes in climate- and production scenarios influence ice formation on small scale and also how future ice scenarios may influence the operation of hydropower plants.

METHODS

Historical data for ice formation and breakup from the Norwegian Water Resources and Energy Directorate is combined with observation data on climate and discharge to study trends in ice regimes in 25 rivers and lakes distributed across Norway, and how freeze-up and breakup is related to climatic and discharge conditions in the rivers. Further, downscaled regional climate scenarios (gridded with 1 km² resolution) from the MPI and Hadley climate models (Engen-Skaugen, 2007) are used to develop scenarios for the length of the future ice season and on the potential for winter thaws which could induce winter ice runs.

The MIKE11 model with the Lasalle ice model is used to study ice formation in the regulated Orkla river in middle Norway. Using the model we simulate ice formation on small scale with the current climate and production regime, and scenarios with future climate regimes using downscaled data and hydropower operational scenarios. Of particular interest here is production scenarios linked to load balancing in a future energy system with increasing non-storable renewable production. The study site in Orkla is a 22 km long reach between the outlet from the Grana power plant and the intake for Svorkmo power plant. The model is driven by observed discharge from the power plants, measured temperature downstream the Gana outlet and climate data from a project operated station close to the Grana outlet. The model is calibrated against observed water level at Syrstad and three temperature stations distributed along the reach. The ice simulation is verified against field observation both from ground based campaigns and from aerial photography.

RESULTS

Results from the analysis of the available ice record for Norway show no clear overall trend in breakup or freezeup dates (Gebre and Alfredsen, 2011). A serious problem with the available data is that most
stations (particularly river stations) ends in the early eighties and thereby misses the period where we see the clearest trend in temperature. Developing river ice forcings from the climate scenarios we see clear increases in temperature and precipitation over the winter months, and also an increase in the number of mild episodes during winter (Figure 1). This indicates possibilities for more winter breakups and a more unstable ice regime in the future, which could have significant implications for infrastructure and winter utilisation of rivers and lakes. From this it also follows that winter runoff will increase for most watercourses.

To study impacts on ice formation on small scale the MIKE11-ice model was calibrated against observed data and then run for various scenarios. Figure 2 shows a comparison of current conditions, a simulated unregulated case using the same climate and a scenario where the Grana plant is stopped and only discharge from the upper Bratset plant is included. The simulation shows increased production of frazil ice in the unregulated case, and also formation of a permanent ice cover at a much earlier stage.

Figure 1 Changes in mid winter thaws from reference period (1961-90) into the future using downscaled climate scenarios

Figure 2 Simulation of ice formation in river Orkla comparing current regulated flow regime, a simulated unregulated regime and a more intermittent production regime.
The simulation data also shows clearly the influence from the hydropower operation on the river ice regime which keeps most of the 22 km of river open all winter and increases the production of frazil and anchor ice compared to the unregulated situation.

CONCLUSIONS AND FURTHER WORK

Updated data on river ice phenology for Norway is not readily available and this makes studies of impacts of recent temperature trends on ice processes difficult. Work is therefore carried out to see if data from satellites can be used to extend existing data series on ice until today or if other sources of breakup data may exist.

The ice modelling shows good agreement with observed ice formation in the river regarding sites for frazil formation and extent of ice covers. No data is available for checking the quantitative output from the model, particularly frazil ice volumes. We intend to collect such data using a Shallow Water Ice Profiler and also collect data on ice growth and floe size to further verify the model. The model will then be used to simulate future flow scenarios based on downscaled climate and future production regimes.

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REFERENCES

INTRODUCTION

Iceland is a major source of dust emissions into the atmosphere over the North-Atlantic Ocean, and has a major controlling impact on ecosystems in Iceland (Arnalds, 2010). There are three major types of areas that can be identified as major dust sources: i) continuous sandy desert areas (total of about 20 000 km$^2$); ii) confined dust plume areas with finer sediments than the continuous sandy deserts, hence more dust production per unit area; and iii) temporary areas created by volcanic eruptions or catastrophic floods in glacial rivers. The unstable tephra fields resulting from the Eyjafjallajökull eruption in 2010 are an example of temporary areas. The confined dust-plume areas in Iceland are most likely among the most active dust sources in the world per unit area. At least seven major such sources have been identified which emit dust plumes up to several hundred km from the dust sources. There are also numerous smaller ones (< 1 km$^2$) which also contribute to the dust emissions. This paper presents an overview of the dust plume areas in Iceland, the distribution of dust deposition and some effects on Icelandic ecosystems. This paper is based on research published by Arnalds (2010) and additional unpublished research.

METHODS

The methods for identifying the dust emissions were primarily three: i) field observations and mapping which conducted during the National Assessment of Soil Erosion in Iceland in the scale of 1:100 000 (Arnalds et al., 2001); ii) systematic scanning of MODIS satellite imagery since 2007 to this date (Figure 1); iii) observations made by the author during > 25 field seasons on various projects related to soil, erosion and restoration. All areas identified as major plume areas in the field were confirmed by major plume activity on MODIS imagery.

Depositional areas (direction from plume sources) for each of the plume source area were determined based on prevailing dry winds patterns within each area, topography (mountain ranges) that affects wind patterns, distance from source and evidence of plume directions on MODIS imagery.

A map was produced for aeolian deposition for all Iceland. It combines the maps made for distribution from each major dust source (plume area) and the sandy areas and data for deposition provided by soil profile measurements. Employing ‘tephrochronology’, the rate of thickening of the soils due to aeolian deposition (in mm/yr) can be determined. The organic content of the soils (measured as % carbon) needs to be subtracted and knowing the bulk density of the soil (g/cm$^3$), the amount of mineral matter between tephra layers of known age can be determined. Using the timeframe provided by the tephras, deposition in g/m$^2$/yr can be obtained. The Agricultural University soil database together with other published research was used obtain deposition rates around the country. Subsequently, a GIS system was used to create a deposition isopach map, utilizing four deposition classes, ranging from low (10-50 g/m$^2$/yr) to very high (>250 g/m$^2$/yr).
RESULTS / CONCLUSIONS

Examples of dust plumes from major dust-plume sources are shown in Figure 1. As can be seen, the dust sources appear point-sources, and the plumes extend several hundred km from the sources. Surface wind speeds are near 20 m/s (10 m height).

Figure 1. To the left is a dust-plume extending from Dyngjusandur in Northeast Iceland, more than 200 km to the ocean. Dyngjusandur represents the largest dust-plume source area in Iceland. To the right are several plumes extending >400 km into the ocean south of Iceland. Both are MODIS images.

The location of the major dust-plume sources are shown in Figure 2. The sources are labelled 1-7 with some of the smaller ones marked 8-12. The major areas affected are the shaded areas. The far largest area is dust-plume source no 1, Dyngjusandur (see also Figure 1). Most of these sources are associated with glacial margins and floodplains. Dyngjusandur is an area that becomes flooded by daily fluctuations in glacial river flow during peak summer melt. Others such as Mýrdalssandur (no 3; Leirá/Múlakvísl/Blautakvísl rivers) and Skeiðarársandur (no 7) are both influenced by seasonal peak flows and catastrophic flooding events. The flooding leaves loose silty and fine sandy materials on the surface, which is easily picked up by moderated winds (threshold 6-8 m/s at 2 m height), but create huge dust plumes during high winds (e.g., > 15 m/s).

The dust plumes are easily carried several hundred km over land and oceans, as frequently revealed by MODIS imagery.

An aeolian dust deposition map is presented in Figure 3. It shows areas of relatively low deposition rates away from the active sources, 10 – 50 g/m²/yr, but very high rates close to the sources of > 250 g/m²/yr. Rates of > 800 g/m²/yr have been calculated near the sources. These are among the highest numbers recorded for the other dust zones on Earth according to review presented by Lawrence and Neff (2009). These numbers place the Icelandic dust sources among those of highest deflation rates, but such areas were surveyed by Washington et al. (2006). This also indicates that Icelandic dust should have a significant effect on climate in the region, as well as on health during dust events.

The volcanic eruption in Eyjafjalljökull resulted in large areas with unstable volcanic tephra on the surface. The first summer after the eruption, massive dust storms occurred which masked out the effect of the permanent dust sources. This clearly demonstrates that events such as eruptions need to be factored in when interpreting the sediment records to obtain mean sedimentation rates.
The fresh materials deposited on soil surfaces weather ‘rapidly’ and release basic cations such as calcium. This maintains relatively high pH in Icelandic soils, especially in the areas close to the sources (pH > 6). The higher pH influences carbon dynamics of the areas and the ecosystems in general, favouring more fertility relatively close to dust sources. The dust is also deposited over oceans with possible influences on marine ecosystems in the North-Atlantic. Furthermore, the dust is deposited on the Icelandic glaciers, lowering their albedo and thus, accelerating glacial melt, further enhancing the effect of global warming.
REFERENCES


CHARACTERIZATION OF A BUBBLE TANK FOR SEA SPRAY AEROSOL STUDIES

M. BILDE¹, A.C. BUTCHER¹, S.M. KING¹, T. ROSENØRN¹, G. DE LEEUW², ESTHER COZ, and E. D. NILSSON⁴

¹Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark
²Finnish Meteorological Institute, FI-00101, Helsinki, Finland,
³Departamento de Medio Ambiente, CIEMAT, E-28040 Madrid, Spain
⁴Department of Applied Environmental Science, Stockholm University, S-10691 Stockholm, Sweden

Keywords: Marine Aerosols, CCN, Organic enrichment, laboratory studies.

INTRODUCTION

Sea spray aerosols (SSA) are of major interest to global climate models due to large uncertainty in their emissions and ability to form cloud condensation nuclei (CCN). SSA may be of particular significance in Arctic climates, where a relative lack of aerosol particles upon which clouds can form suggests that small changes in aerosol loading may lead to large changes in the warming potential of Arctic clouds and the subsequent ice-melt. (Maurtisen et al. 2011). In general, SSA are produced from wind breaking waves that entrain air and cause bubble bursting on the ocean surface, but the exact mechanism producing particles and governing their organic enrichment is poorly understood. The size of SSA ranges from tens of nanometers to hundreds of microns, with possibly more than 90% of the particle number in the submicron range (Fitzgerald 1991). There is a lack of consensus on the size spectra below 200 nm, and as a result, they are not well represented in current parameterizations (Nilsson et al. 2007, O’Dowd et al. 2008, Pierce and Adams 2006, Russell and Singh 2006). A detailed review of the current state of knowledge about sea spray aerosol production flux and its representation in aerosol models can be found in de Leeuw et al. (2011). Preliminary results are presented here for bubble generation, bubble size distribution, and particle size distribution for laboratory generated SSA.

METHODS

It has been suggested that a plunging jet, formed by a continuously flowing nozzle placed vertically above a water surface, closely resembles breaking-wave bubble entrainment processes and subsequent bubble size distributions (Fuentes et al. 2010, Lewis and Schwartz 2004, Hultin et al. 2010). The experimental equipment consists of a stainless steel cylinder closed at both ends with ports for aerosol sampling and air supply. Bubble generation was implemented with a recirculating jet with 16-mm or 4-mm nozzles or a stainless steel frit. Particle size distributions were measured with an SMPS and CCN activity of the particles was measured using a DMT CCN counter. Figure 1 shows size distributions measured for particles produced under varying methods of bubble generation. The range of size distributions of particles produced from bubbles generated with air flow rates of 3.0 to 10.0 L min⁻¹ through the frit, placed at a depth of 29 cm, are shown in light red in Figure 1. Particle distributions produced with the recirculating jet, where the flow rate of 4 and 16 L min⁻¹, are shown in gray. In general, particle concentrations achieved using the jet are an order of magnitude lower and with less pronounced peaks than with the frit. The smaller number of particles generated can be attributed to the turbulent bi-phasic flow near the jet centerline which may disrupt bubble-bursting processes (Fuentes et al. 2010). However, the disruption of the bubbles may not be enough to significantly reduce the particle concentration, and an additional cause may be the high entrainment rates of the plunging jet itself (Bin 1993). Particles were also collected on a filter and analyzed for morphology using Scanning Electron Microscopy.
Figure 1. Particle Size Distributions from several bubble generation techniques. Light pink regions indicate the range of frit size distributions from 3.0 L min\(^{-1}\) to 10.0 L min\(^{-1}\) air flow. Gray region shows the plunging jet under different flow conditions.

The bubble size distribution formed by the various bubble generation techniques has been performed using the mini-BMS system (Leifer, de Leeuw and Cohen 2003). Figure 2 shows the bubble spectra for several of the bubble generation techniques employed in this study. The bubble size distribution can be used as an indication of similarity of laboratory studies to oceanic conditions. Power laws for the bubble size distributions that are found in oceanic whitecaps (Lewis and Schwartz 2004) are shown as straight lines on the log-log plot.

Figure 2. Bubble size distribution results from various bubble generation techniques with common roll off power laws shown.
In addition to particle size distributions and bubble spectra, we also measured the CCN activity of the particles produced via bubble bursting processes and an atomizer. A comparison of CCN activity is shown in Figure 3 between sodium chloride, artificial sea salt purchased from Tropic Marin, and laboratory grade artificial sea salt (Kester et al. 1967).

Figure 3. CCN activity of sodium chloride, artificial sea salt, and Tropic Marine Sea Salt, both for atomized and bubbled experiments.

Determination of particle morphology is essential in accurate interpretations of data measurements involving the use of a DMA, which classifies particles by electrical mobility and whose performance is defined for spherical particles. In this study, AR is not converted to corresponding $\chi$ values; instead, they are provided solely for intercomparison. For reference, AR values for PSL spheres verify that they are the most spherical of the samples analyzed. Further results in Table 1 indicate that atomized NaCl particles are less cubic than atomized sea salt and mixed particles. Due to the uncertainty in the AR values, conclusions regarding the potential morphological differences between mixed sea salt-organic particles and pure sea salt particles are not possible.

One explanation for the higher observed AR values for sea salt particles is the higher apparent incidence of twinning, or aggregation, of single particles. The only sample population in which aggregation is nearly absent is that of polydisperse NaCl particles. Between 25 to 35% of the particles in the remaining samples comprised two or more crystals, implicating twinning.
Table 1. SEM aspect ratio results from SEM image analysis.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Mean aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 60-nm PSL spheres</td>
<td>1.09 ± 0.006</td>
</tr>
<tr>
<td>2. Artificial seasalt (TMSS)</td>
<td>1.28 ± 0.016</td>
</tr>
<tr>
<td>3. SS:Sodium palmitate (3500:1)</td>
<td>1.26 ± 0.016</td>
</tr>
<tr>
<td>4. SS:Fructose (100:1)</td>
<td>1.30 ± 0.018</td>
</tr>
<tr>
<td>5. Polydisperse NaCl particles</td>
<td>1.20 ± 0.024</td>
</tr>
<tr>
<td>6. 100-nm NaCl particles</td>
<td>1.24 ± 0.014</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The larger aspect ratio of sea salt particles may partially explain the difference in its CCN activity from that of pure NaCl. Further study at much lower organic concentration is needed in order to probe organic enrichment from bubble-bursting. Issues such as shape factor and measurement precision lead to difficulties in CCN data interpretation. The temperature of the artificial sea water and air entrainment properties of the jet will also be investigated for their effect on particle production and CCN activity.

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REFERENCES

THE IMPACT OF VOLCANIC TEPHRA AEROSOLS ON GLACIER MELTING

H. BJÖRNSSON¹, S. GUÐMUNDSSON¹, F. PÁLSSON¹, E. MAGNÚSSON¹, TH. THORSTEINSSON¹
AND H. H. HANNESSON²

¹ Institute of Earth Sciences, Science Institute, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland.
² National Power Company of Iceland, Háaleitisbraut 68, 103 Reykjavik, Iceland

Keywords: GLACIER MELTING, VOLCANIC TEPHRA, AEROSOLS

OBJECTIVES

Observations of the distribution volcanic ash over glaciers in Iceland during and after the abrupt eruptions of Eyjafjallajökull (2010) and Grímsvötn (2011) provide valuable experimental data for studies of the impact of the depositions of aerosols on radiative forcing in Arctic regions and speed up of snow and glacier melt. 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; Guðmundsson et al., 2009). Satellite observations of glacier surface albedo can be calibrated and verified by ground based observations of dust and ash dispersion (mobilization) and deposition on glacier/snow surfaces during the eruptions.

INTRODUCTION

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 (Figure 1). After the 2010 eruption, the entire Eyjafjallajökull ice cap and most of the neighbouring Mýrdalsjökull, were covered with a thick ash layer which insulated the ice and snow surface from atmospheric energy fluxes, 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 2a and Figure 3). Similar contrasting conditions were observed after the 2011 eruption of Grímsvötn in Vatnajökull; areas close to the eruption site were covered with a thick insulating tephra layer (Figure 2b).

Figure 1. The plume from the Eyjafjallajökull eruption. a) The tephra was blown towards the south and southeast during a prolonged period of northern and western winds. b) MODIS image from 18 May 2010. Albedo dropped on Langjökull, Hofsjökull and Vatnajökull ice caps (location in Figure 2) between 18-20 May during southern and southwestern winds.
Figure 2. a) MODIS image from 9 August 2010. After the 2010 eruption, a thick insulating tephra layer covered Eyjafjallajökull (E) and Mýrdalsjökull (M). Most of Vatnajökull (V), Hofsjökull (H) and Langjökull (L) covered with thin a tephra layer. b) MODIS from 10 August 2011. Thick insulating tephra covered SV-Vatnajökull and thin layers the other ice caps.
CONCLUSIONS

COLLECTION OF MASS BALANCE AND METEOROLOGICAL DATA

The mass balance has been observed at 40-60 sites on Vatnajökull since 1992 and at 22-23 sites on Langjökull since 1996 (Figure 4). During the summers since 1994 automatic weather stations (AWSs) at 2-10 locations on Vatnajökull and 2-3 stations on Langjökull (since 2001) (Figure 4), have monitored at 10 minutes interval all the meteorological parameters needed to calculate the glacier surface energy balance (Figure 5).

PRELIMINARY RESULTS

The mass- and energy balance observations from 2010 on Langjökull and Vatnajökull are 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 (Figures 6) 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 (Figure 7). 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.
Figure 4. Red circles: location of the mass balance sites on Langjökull (L) and Vatnajökull (V). Black triangles: location of the automatic weather stations 2010 (typical setup in Figure 5).

Figure 5. Automatic weather station on the glacier. The instruments are mounted on a mast, standing on four feet, following the surface while melting. The station measures directly the incoming ($Q_i$) and outgoing ($Q_o$) solar radiation, incoming ($I_i$) and outgoing ($I_o$) long wave radiation, and temperature (T), humidity (r) and wind-speed (u) at one to four levels above the surface. In addition, the daily melting rate was measured directly, using sonic echo sounder mounted on a mast drilled into the surface.
Figure 6. Langjökull ice cap at 1100 m a.s.l. close to the average ELA. The frames show daily values of the continuous ablation, albedo and total energy supplied for melting; separated into contributions from net radiation and turbulent heat fluxes. The thick red lines show the results from the summer 2010, and they are compared to values from summers of 2001-2009. The albedo dropped 18 May when tephra was blown over the surface (three days before the end of the eruption; Figure 1). The low albedo led to exceptionally high net radiation balance of the glacier surface and high melting rate. The sensible and latent heat fluxes were close normal albeit the summer 2010 was one of the warmest recorded in Iceland.
Figure 7. Specific mass balance of the Vatnajökull and Langjökull ice caps. Due to low albedo of the glacier surface (Figure 6), magnifying the melting, the net mass balance of the year 2010 was ~3 times lower than during the warm period after 1996.

REFERENCES


INTRODUCTION

The role of atmospheric aerosols is perhaps the biggest unknown concerning our climate and greenhouse warming (IPCC, 2007). New particle formation has been observed at almost all sites, where particle size distributions have been measured. Although many field campaigns, laboratory experiments and new modeling approaches have led to increased understanding, detailed mechanisms responsible for the formation of new particles in the troposphere have still not been completely elucidated. One of the most controversial topics is the role of organic against sulfuric acid molecules in the formation process.

METHODS

In this study we present results achieved by two models: MALTE (Boy et al., 2006) and SOSA (Boy et al., 2011). The meteorology in both models is based on a 1-D version of the model SCADIS (Sogachev and Panferov, 2006) and the Model for Emissions of Gases and Aerosols in Nature (MEGAN) is used to simulate the emission of organic vapors from the biosphere. The gas phase chemistry is solved with the Kinetic Pre-Processor (KPP) in combination with the Master Chemical Mechanism from the University of Leeds. SOSA in contrast to MALTE is a parallelized model operating on the high-performance supercluster Murska at the CSC - IT Center for Science in Finland, which gives the possibility to run detailed processes in chemistry, aerosol dynamic and meteorology over long periods with reasonable model runtime.

CONCLUSIONS

We will present different model results in comparison with measurements aiming to demonstrate or even increase the controversial discussion about the role of organics against sulfuric acid when considering the question: What are the crucial molecules for new particle formation in the atmosphere?

One possible way to get some hints to solve this question is the use of long-term comparisons between different parameters simulated with the new model SOSA and the frequency of particle formation events (Boy et al., 2002). In this context we calculated different combinations of parameters like e.g RP-1:

\[ RP-1 = \frac{[H_2SO_4]}{CS} \]

the concentration of sulfuric acid divided by the condensation sink of the pre-existing aerosols.

Figure 1 presents the number of event days in three different classes (Boy et al., 2002) and the amount of days per month where the daytime (9-15) mean value of RP-1 exceed the mean value calculated over the years 2003-2008 by 0, 10, 25 %, respectively.
Figure 1: Monthly trend for RP-1 and observed frequency of nucleation event days

The figure shows a clear correlation in monthly distribution between sulfuric acid and nucleation event frequency. Including the monoterpenes, temperature and water vapour into the equation shifts the distribution more towards the summer months but also decrease the amount of days during the second observed event peak in autumn.

In figure 2 vertical profiles for the sum of monoterpenes, hydroxyl radicals and sulfuric acid predicted by SOSA for the 26\textsuperscript{th} of March 2003 at 11.25 are shown. Both compounds, H\textsubscript{2}SO\textsubscript{4} and OH present a similar trend with nearly constant values up to about 300 m. Above and up to 2150 m both compounds decrease by ca. 50 % and start to increase afterwards. The sum of the monoterpenes showed a completely different profile, which is expected from a substance emitted by the canopy. The concentration is well mixed inside the ABL - due to clear sky condition on this day and the resulting strong turbulence - and decreases continuously to values below 100 molecules cm\textsuperscript{-3} above 2 km.

Figure 2: Vertical profiles of simulated OH-, sulfuric acid and sum of monoterpenes concentrations for the 26\textsuperscript{th} of March 2003 at 11.25 am.

Comparing the measured particle concentrations in the size range of 3-6 nm for this selected day and time (high numbers of new formed particles of several thousand inside the ABL and numbers under the detection limit above, O’Dowd et al., 2009, Figure 9) with the simulated profiles of sulfuric acid and monoterpenes, a higher similarity for the organic vapor concerning the vertical distributions could
be identified. This could be strong evidence that the amount of new formed particles detected at sizes above 3 nm are more related to the concentrations of organic molecules than to the concentrations of sulfuric acid inside and above the ABL.

Facing the strong different opinions in the aerosol community about what molecules are responsible for the formation of new particles in the atmosphere (e.g. Boy et al., 2008) – organics or sulfuric acid – we compared vertical profiles for both compounds with measured particle concentrations between 3-6 nm and performed statistical long-term analysis of simulated sulfuric acid concentrations and other parameters. Although these results could not give any information about the processes involved, it is notable that both sulfuric acid and the organic molecules give reasons why they can be considered as crucial when we talk about new particle formation. Although our understanding on this topic has increased dramatically during the last decades the final knowledge which molecules are the key ones is still missing.

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REFERENCES

EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM A BOREAL HUMIC LAKE

J. BÄCK¹,³, A. OJALA², J. PUMPANEN³, H. SJÖBLOM², H. AALTONEN³,⁴, H. HAKOLA⁴, and H. HELLEN⁴

¹Department of Physics, University of Helsinki, Finland
²Department of Environmental Sciences, University of Helsinki, Finland
³Department of Forest Sciences, University of Helsinki, Finland
⁴Finnish Meteorological Institute, Finland

Keywords: VOLATILE ORGANIC COMPOUNDS, LAKE EMISSIONS, PHYTOPLANKTON

INTRODUCTION

The aquatic sources of volatile organic compounds to atmosphere have been mainly studied in marine environments. Marine phytoplankton is producing e.g. dimethylsulphopropionate which is converted by bacteria to dimethyl sulfide, which is a very effective contributor to particle formation in marine environments. Also isoprene and some organic acids have been measured from oceanic sources (Colomb et al 2008, Yassaa et al 2008). However, lakes comprise large inland areas in Scandinavia, and their potential contribution to atmospherically reactive compounds has not been analyzed. We designed an experiment where the emission spectrum and emission rates from a humic southern Finnish lake were followed over one summer period.

METHODS

We measured the emissions of isoprenoids and short—chained carbohydrates from a raft located in the middle of Lake Kuivajärvi, close to the SMEAR II station in Hyytiälä, southern Finland.

FIGURE 1. The measurements were located on the raft.
Air entering and leaving a floating, teflon-coated enclosure was sampled to adsorbent tubes (Tenax TA) or to a sampling canister. The enclosure was flushed for 30-60 min before the sampling, which took 3-4 hours, always at noon. The emission measurements were combined with those of water temperature, light penetration, chlorophyll, CO$_2$ and O$_2$ concentrations, and phytoplankton populations. VOC analyses were performed at the Finnish Meteorological Institute with GC-MS after thermodesorption (Hakola et al. 2006). Canister sample air was concentrated with liquid N traps and analyzed with GC-FID (Hakola et al. 2003). Simultaneously with the gas samples also plankton samples were collected and their species composition was analyzed later in the laboratory under microscope. Phytobiomass was analyzed using chlorophyll determination with a spectrophotometer.

RESULTS

The summer 2010 was exceptionally warm in Hyytiälä. The surface water temperature reached 22 °C in mid July, creating an 18 °C temperature gradient between the bottom and surface of the lake.

The lake VOC flux varied a lot within the summer. Terpenoid emissions increased during the summer and declined rapidly after mid-August. The three most abundant compounds in emissions were $\alpha$-pinene, $\Delta^3$-carene and p-cymene. Also the limonene emissions were quite high. Some sesquiterpenes (most abundantly $\beta$-caryophyllene) were also seen in the emissions, although generally their emission rates were very low.

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<td>723</td>
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<td>27</td>
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<td>p-cymene</td>
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<td>205</td>
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<td>366</td>
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<td>34</td>
<td>24</td>
<td>6</td>
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<tr>
<td>limonene</td>
<td>97</td>
<td>165</td>
<td>157</td>
<td>423</td>
<td>NA</td>
<td>NA</td>
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</table>

**SUM Monoterpenes** 1688 1732 2138 1920 2993 299 849

| iso-longifolene | 0 | 0 | 0 | 3 | 0 | 1 | 1 |
| $\beta$-caryophyllene | 0 | 6 | 13 | 4 | 3 | 10 | 5 |
| $\alpha$-humulene | 0 | 0 | 0 | 0 | 0 | 0 | NA |
| alloaromadendrene/farnesene | 0 | 0 | 0 | 6 | 0 | 0 | NA |

**SUM Sesquiterpenes** 0 6 13 14 3 12 6

Table 1. Most abundant mono- and sesquiterpene emissions (ng m$^{-2}$ h$^{-1}$) from Lake Kuivajärvi in summer 2010. NA = not analyzed
The emission dynamics of short-chained hydrocarbons was somewhat different from that of isoprenoids. The maximum emissions were measured in early summer, and emissions declined towards the fall. The most abundant compounds were ethane, ethene and propene.

<table>
<thead>
<tr>
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<td>2</td>
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<td>propane</td>
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<td>NA</td>
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<td>190</td>
<td>102</td>
<td>NA</td>
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<td>65</td>
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<td>NA</td>
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<td>22</td>
<td>20</td>
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<tr>
<td>propyne</td>
<td>82</td>
<td>22</td>
<td>NA</td>
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</tr>
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<tr>
<td>cis-2-pentene</td>
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<td>0</td>
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<td>1783</td>
<td>943</td>
<td>739</td>
<td>289</td>
</tr>
</tbody>
</table>

Table 2. Most abundant aliphatic and cyclic short-chained hydrocarbon emissions (ng m$^{-2}$ h$^{-1}$) from Lake Kuivajärvi in summer 2010. NA = not analyzed

CONCLUSIONS

The VOC emissions from a humic lake in southern Finland were rather high, up to 3 µg m$^{-2}$ h$^{-1}$, which is comparable to emissions from forest soil and belowground vegetation (Aaltonen et al. 2010). Also the compound spectrum resembled the emission spectrum from terrestrial environments with highest fluxes of Ï- pinene and carene. p-cymene emissions were also relatively high throughout the summer. Temperature seemed to correlate well with the emissions of monoterpenes ($r=0.74$). The total phytoplankton biomass and the biomass of Gonyostomum semen correlated with the emissions of camphene and Ï-pinene ($r = 0.3 \ldots 0.5$) and butane and ethene ($r = 0.3 \ldots 0.6$). The biomass of Urosolenia longiseta (Zacharias) correlated with camphene and carene emissions ($r = 0.4$).

Our next step is to analyze the emission patterns in more detail, and especially study the seasonal variability in emission patterns during the whole ice-free period. We also aim at connecting the emissions with lake biological activity and other variables, i.e. CO$_2$ fluxes, phytoplankton speciation and levels of dissolved organic matter.

ACKNOWLEDGEMENTS

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REFERENCES


THE IN-SITU OBSERVATIONS OF PARTICLE TRANSPORT PROCESSES NEAR EYJAFJALLAJÖKULL VOLCANO AFTER THE 2010 ERUPTION

P. DAGSSON WALDHAUSEROVA1,2, O. ARNALDS1, J. ÞÓRSSON2 and E.F. ÞÓRARINSDÓTTIR2

1 Faculty of Environment, Agricultural University of Iceland, Hvanneyri, Borgarnes, IS 311, Iceland.
2 Soil Conservation Service of Iceland, Gunnarsholt, IS 850, Iceland.

Keywords: VOLCANIC ASH, DUST STORMS, SALTATION, WIND EROSION

INTRODUCTION

The Icelandic volcano Eyjafjallajökull started erupting in spring of 2010 with a strong volcanic explosion occurring on 14th of April 2010. The ash plume reached over 9 km height and reached 155 km distance from volcano (Arason et al., 2011). The fine-grained volcanic ash particles were released into the atmosphere and dispersed globally (Stohl et al., 2011). The interaction of magma and ice augmented explosive activity and generated large proportions of fine ash that were emitted into the atmosphere (Gudmundsson et al., 2010). Intense tephra discharge continued for several days and the Nordic Volcanological Institute reports 100 million m³ of tephra was ejected (Arason et al., 2011). The summer of 2010 was dry with frequent occurrence of high winds, resulting in numerous wind erosion events. The dust was carried several hundred km during the most intense events and air quality was severely affected in much of South and Southwest Iceland during these storms.

Dust deposition from a range of dust sources in Iceland affects much of Icelandic ecosystems in general (Arnalds, 2010). The Eyjafjallajökull eruption added a new source of aeolian materials, which remained very active the first year. The Soil Conservation Service of Iceland and the Agricultural University of Iceland conducted in-situ measurements of the particle movement at several locations in the affected areas. Measurements were carried out on transport but also meteorological elements. Air quality was measured at several locations by the Environmental Agency of Iceland.

In this paper a general description of the methods used to measure aeolian transport of the volcanic materials and preliminary results are provided together with examples of the storms. An attempt is made to relate the results to measurements of air quality.

METHODS

Instrumentation was placed at two general locations within the areas affected by volcanic deposition. The sites were Skógahreit, SE of the volcano, and Fljótshlíð, N of the volcano. At each site, BSNE wind erosion samplers developed by Fryrear (1986) were placed several locations, 30 cm and 60 cm above the surface. In addition, there was one set of 5 samplers placed at 10, 30, 60, 90, and 120 cm height at the same location. Two setups of automated wind erosion counters (SENSIT) were used, one at each side of the volcano. These instruments are programmed to give a pulse upon an impact from moving grains using piezo-electric material. These pulses are magnified and counted. At each site, weather parameters, such as temperature, relative humidity and wind speed (2 m height) were measured simultaneously with impact counts, allowing for relating wind speeds and wind erosion intensity. The samplers give a better overview
of total particle movement (erosion), while the data generated by the automatic sensors are ideal to study the characteristics of each storm. The dust traps were emptied after each storm period, a total of 13 periods. A characteristic height distribution curve for each location obtained by the set of 5 samplers placed at different heights was used to calculate transport for each period where only one sampler was in place. The unit of measurement is amount of material transported over 1 m wide transect (kg/m) in total or per unit time (kg/m/hr; kg/m.minute).

CONCLUSIONS

The Eyjafjallajökull eruption in Iceland in 2010 provided a unique opportunity to study volcanic ash transport in natural environment. Within five months from June 2010, we had observed over 30 moderate to severe dust storms with maximum wind speed of 38.7 m/s. The maximum saltation counts by the electronic instrumentation were 6825 pulses per minute, which is the highest we have measured during the 16 years of operation of the instrumentation at various locations. The mean grain size of the particles moved and sampled in BSNE erosion samplers range from 0.13 to 0.69 mm, and grains > 2 mm were moved during the most intense storms.

The vertical particle size analysis represents different distribution of particles during moderate and severe wind erosion events. During moderate events, 90% of the material is concentrated in the saltation layer up to 45 cm above surface. Contrarily, during severe events the same proportion increases the height of the saltation layer to 85 cm above surface. There is a significant increase in proportion and mass of particles larger than 2 mm with the heights with increasing intensity of storms. After severe storms, particles < 0.125 mm were not found in samplers at all heights and during moderate events particles > 1 mm were not moved in saltation. We infer that there is a sorting of surface materials during the early storms with the finer materials being lost into the atmosphere while larger particles still remain at the sites.

Figure 1. Dust pollution in Reykjavik after the Eyjafjallajökull eruption. Reykjavik is about 150 km from the volcano. The graph shows PM10 pollution. Source: The Environment Agency of Iceland, Þorsteinn Jóhannsson. Used with permission.
An example of the dust pollution created by the Eyjafjallajökull dust storms is presented in Figure 1, reaching 800 µg/m³ in early September 2010. The pollution closer to the volcano reaches far higher numbers.

At some of the sites, threshold velocity of wind erosion increased from about 10 to 18 m/s during the study period. During the severe dust storm, the saltation intensity increases exponentially with average wind speed to the saturation point and then grows gradually (Figure 2). The saltation saturation point in natural environment at Eyjafjallajökull is 24 m/s wind speed and 5 500 pulses per minute saltation.

![Figure 2](image_url)

Figure 2. Two different storms measured at Eyjafjallajökull in July and September 2010. The x-axis represents wind speeds in meters per second and the y-axis the saltation in pulses per minute.

The dust from Eyjafjallajökull affects the ecosystems over much of Iceland, providing new, un-weathered materials on the surface. It is likely to affect the ecosystems of the oceans around Iceland, and it brings dust that lowers the albedo of the Icelandic glaciers, increasing melt-off during times of global warming.

ACKNOWLEDGEMENTS

This work was supported by the Soil Conservation Service and Agricultural University of Iceland.

REFERENCES


INTRODUCTION

Black carbon aerosol, or soot, is transported to the Arctic from densely populated areas in lower latitudes. Due to their high absorption cross section soot particles have a lowering effect to the Arctic surface albedo and thus enhance melt. Transport and deposition processes, especially latter, are not sufficiently studied to understand the spatial and temporal distribution of soot in Arctic snow.

Svalbard, an archipelago situated in the European Arctic between latitudes 74 and 8° N receives most of its precipitation as snow and often during easterly flow. Transport of various contaminants are estimated to have mainly European and Asian source, while westerly flow appears cleaner from pollution (Forsström et al. 2009, Ruggirello et al. 2010). The topographic effect of the mountainous islands and valleys largely covered with glaciers complicate the deposition processes.

METHODS

Snow samples including both surface samples of topmost 5 cm and column samples through the whole annual snow back were analyzed for soot using thermal optical method (NIOS 5040 protocol). Samples were collected as matter of opportunity at eight locations around Svalbard during the spring seasons of 2007-2010. Samples together with measurements of annual snow accumulation show a strong link between the soot flux (g/(m² year)) and precipitation amounts.
RESULTS AND DISCUSSION

Eastern Svalbard receives more of the soot arriving from European and Asian sources than the western Svalbard. In addition to the archipelago-scale (~100 km) mapping of soot in snow, small scale case studies (scales of 10 km) and studies of 1 m scale variability of the contaminant in snow are included.

REFERENCES


Aerosol particles in the atmosphere influence the Earth’s radiation balance directly by scattering or absorbing incoming solar radiation (e.g. Kahn et al., 1998; von Hoyningen-Huene et al., 2011) or indirectly by influencing the properties of the clouds that are formed on the particles (e.g. Twomey, 1977; Twomey et al., 1984; Charlson, et al., 1992; Glantz et al., 2000). It is well established that the generation of sea salt aerosol is strongly dependent on the surface wind speed (e.g. O’Dowd et al., 1997; Nilsson et al. 2001; Glantz et al., 2004). It has also been suggested that the impact on climate may change the primary marine aerosol production significantly, either through changes in surface water temperature (Mårtensson et al., 2003), or wind speed (Latham and Smith, 1990). In a recent study, Young et al. (2011) actually have found a general global trend of increasing wind speed for the period 1991-2008. In addition, Korhonen et al. (2009) concluded that sea salt aerosol concentrations in the atmosphere at southern mid-latitudes (50-65°S) may have increased by 22% from the 1980s to present day, although here primarily due to changes in surface winds driven by the development of the Antarctic ozone hole. Relationships between ground as well as satellite retrieved aerosol optical thickness and surface wind speed have been found by for the Northeast Atlantic (Mulcahy et al., 2008) and central North Pacific (Glantz et al., 2009), respectively. In both studies sea salt is a strong candidate for yielding enhanced scattering of radiation. From the references in the latter study several additional relationships obtained over other ocean regions can be found.

Furthermore, the emissions of sea salt could actually be the dominant source also of cloud condensation nuclei (CCN) particles, especially in remote areas with moderately and high wind speeds and low water temperatures (Pierce and Adams, 2006). Thus, an important negative or positive climate feedback is expected due to changes in the emissions of sea salt. However, while a relationship between simulated CCN and surface wind speed is suggested, observed influences on the cloud properties has not been confirmed. The latter is probably due to, at least partly, thermodynamically effects that also highly influence the boundary layer and clouds present, which then masks the effects of the surface wind speed. Absorption of short wavelength radiation probably also plays an important role in creating turbulence and mixing of air in the boundary layers (Svensson et al., 2000, Glantz et al., 2004).

In the present study (Glantz, 2011) low level liquid stratocumulus (Sc) clouds in the subarctic marine atmosphere have been investigated, on the bases of satellite cloud retrievals and reanalyzes of meteorological quantities, in order to estimate an empirical relationship between cloud optical thickness (COT) and surface wind speed.

METHODS

The satellite cloud product parameters (level 2) COT and effective cloud radius ($r_{\text{eff}}$), from the moderate resolution imaging spectrometer (MODIS) sensor onboard the Aqua satellite, have been analyzed for the Norwegian Sea and Barents Sea for the months March to October and the years 2000 to 2006. The microphysical and optical properties of the clouds (with 1 km horizontal resolution) are derived by
comparing radiation signals from a visible channel (0.86 μm) and infrared channel (2.1 μm) and iteratively lining these up against libraries of pre-calculated values for homogeneous clouds that are plane-parallel (Platnick et al., 2003). To estimate cloud top temperature (CTT) the 11 μm method (used on clouds at pressures above 700 hPa) proposed by Platnick et al. (2003) has been applied to the MODIS data (with ~4 km horizontal resolution). The CTT has been combined with the European Centre for Medium-Range Weather Forecasts (ECMWF) sea surface temperature (SST), shown in Figure 1, to estimate the boundary layer height (BLH_{estim}).

Figure 1. The solid and dashed black lines denote MODIS mean ST and CTT, respectively, and solid and dashed gray lines denote ECMWF mean T_{2m} and SST, respectively, obtained for marine conditions. The error bars denote one standard deviation. Estimated BLH_{estim} and corresponding one standard deviation as well as ECMWF BLH are also shown.

The estimation of BLH_{estim} is used to include only low level clouds (< 1 km) in the present investigation. For this estimate an adiabatic decrease in temperature of 1 K per 100 m is assumed. The higher BLH_{estim} compared to the ECMWF model, particularly for the most shallowest layers shown in Figure 1, is probably explained by underestimated CTT. The latter probably occurs when the 11 μm method is used for the situations with inversion presented. Figure 1 shows good agreement for temperatures estimated at 2 m above the surface (T_{2m}) and at the surface (ST), obtained by the ECMWF and MODIS, respectively. In addition, to exclude too thin clouds, only pixels with COT > 5 (Kokhanovsky et al., 2005) are included here. Finally, pixels flagged as multilayered clouds, containing ice or uncertain cloud phases, were removed as well.

Beside the meteorological parameters in Figure 1 also assimilated fields of 10 m wind speed (U_{10m}) has been analyzed. And the operational meteorological data, with a spatial resolution of 0.25 ° (~17 km), are produced by the ECMWF Meteorological Archival and Retrieval System (MARS). Furthermore, air masses that were only originated south of the area investigated, for the years 2000–2006, have been included. The air mass transport has been identified by NOAA HYSPLIT 4 seven day back trajectories. From this 52 and 30 days have been classified as marine and continental, respectively.

The cloud thickness (H) was estimated using an equation from Bennartz (2007), which has been derived using adiabatic cloud theory:

\[ H = (2 \times \text{LWP}/c_w \text{CF})^{1/2}. \]  
(1)

\[ c_w \] is the condensation rate at 80% of its adiabatic value and is expressed as

\[ c_w = 0.8 \times (1/(R_{H2O} \times T)) \times (\text{dew}(T)/dT) \times (dT/dz) \]  
(2)
where \( c_w \) is the cloud fraction (here set to 1), \( C_f \) is the water vapor pressure, calculated according to a formula given by Emanuel (1994). In addition, \( T \) represents the CTT. Finally, the droplet number concentration \( (N_d) \) obtained for adiabatic conditions by combining equation (1) with the derived column droplet number concentration (Bennartz, 2007):

\[
N_{\text{col}} = \frac{5\tau}{(6\pi \times k \times (r_{\text{eff}})^2)}
\]

where \( \tau \) is COT and \( k \) (the ratio between the volume radius and the \( r_{\text{eff}} \)) is 0.7.

RESULTS

Figure 2 shows the MODIS mean COT and the corresponding one standard deviation as a function of ECMWF \( U_{10\text{ m}} \), averaged according to the 52 days associated with marine air masses. The solid black line shown in the figure is a power fit according to the mean values of COT, and which results in a high \( R^2 \) value. For all cloud pixels (390 373) included in the present study an \( R^2 \) of 0.51 is obtained, according to the relationship COT = 12.2 + 0.081 \( \times U_{1.9} \). The corresponding R value, although quite low, is statistically significant at the 99% confidence level. Beside COT, Figure 3 shows that also MODIS LWP and estimated \( N_d \) increase substantially due to the higher wind speeds, while no statistically significant change in \( r_{\text{eff}} \) occurs.

Figure 2. MODIS retrieved mean COT and the corresponding one standard deviation as a function of ECMWF mean \( U_{10\text{ m}} \) for the marine cases analyzed in the present study.

Figure 3. Estimated mean \( N_d \) and the corresponding one standard deviation as a function of ECMWF \( U_{10\text{ m}} \) for the marine cases. MODIS retrieved mean LWP and \( r_{\text{eff}} \) and the corresponding one standard deviation are also shown.
Table 1 shows results of MODIS cloud retrievals for polluted and clean conditions, obtained in the present work and a previous study (Sporre et al., 2009). The latter study is performed for the same ocean region while for other days than the present work. The table shows that reasonable agreement occurs in estimated $r_{\text{eff}}$. In addition, Table 1 shows that the LWP and COT are substantially higher in the present study. The latter is probably due to differences in air mass transports. In the previous study the clean air masses arrived mainly from north and the polluted ones were transported longer periods over land, before they arrived to the investigated ocean area.

### Table 1. MODIS cloud optical and microphysical parameters

<table>
<thead>
<tr>
<th>Studies</th>
<th>Classification</th>
<th>$e_{\text{eff}}$ ($\mu$m)</th>
<th>LWP (gm$^{-2}$)</th>
<th>COT</th>
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</thead>
<tbody>
<tr>
<td>Polluted</td>
<td>Present</td>
<td>9.74 ±0.94</td>
<td>115 ±44</td>
<td>17 ±6</td>
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<tr>
<td></td>
<td>Sporre et al. (2011)</td>
<td>10.7 ±1.1</td>
<td>82.6 ±25</td>
<td>12.2 ±1.8</td>
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<tr>
<td>Clean</td>
<td>Present</td>
<td>13.42 ±1.54</td>
<td>111 ±31</td>
<td>12 ±3</td>
</tr>
<tr>
<td></td>
<td>Sporre et al. (2011)</td>
<td>14.4 ±1.7</td>
<td>55.0 ±14</td>
<td>5.91 ±0.6</td>
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</table>

**CONCLUSIONS**

Low level marine clouds presented over the Norwegian Sea and Barents Sea has been investigated for the years 2000 to 2006. The more or less northward transports of the air masses, before they arrived to the investigated area, suggest stable stratification in the marine boundary layers and thus minor influence by buoyancy. The latter is supported by ECMWF SST field and low CAPE values found (Glantz et al., 2010). Thus, the investigated shallow marine boundary layers were probably instead to a larger extent affected by wind shears. This means that the observed changes in the cloud properties were probably mainly caused by emission processes at the sea surface and shear-generated turbulence. Consequently, beside higher emissions of sea salt (e.g. O’Dowd et al., 1997; Nilsson et al. 2001; Glantz et al., 2004) and water vapour (Glantz et al., 2009) higher wind speeds also lead to higher updraft and supersaturation, thus, more efficient vertical mixing and activation of hygroscopic aerosols in the marine boundary layer. The relationship between daily mean COT and surface wind speed ($U_{2.5}$) shown in Figure 2 is also in between those most commonly found in the literature for water vapour ($\sim U_1$) and sea salt ($\sim U_{1.4}$).

The results of a correlation between COT and wind speed is very promising in the sense that the latter quantity is probably associated with relatively small uncertainties, at least outside the tropics, in climate model estimations. Thus, the relationship allows a very simple but powerful way to incorporate climate forcing in model predictions. The present results highlight the magnitude of marine sea-spray influence on COT and their global climatic importance.

The differences in cloud microphysical and optical properties between polluted and clean air masses, shown in Table 1, give some support for the satellite retrievals. Even so, based on theoretical arguments and explicit 3-D computations Marshak et al. (2006) find on the other hand substantially overestimations in the retrievals of $r_{\text{eff}}$. In addition, the mean COT estimated here is associated with large error bars for the lowest and highest wind speeds. This seems be due to, at least to some extent, low amount of data available for these wind speed ranges. In addition, large one standard deviations corresponding to the estimated mean $N_d$ are shown in Figure 3, although these values are in any case in the range of droplet numbers observed from aircraft over the warmer northeast Atlantic during clean conditions (Glantz et al., 2003).

Since the space-borne sensors mainly detect the upper part of the clouds, due to a plane parallel model, uncertainties are probably induced in the present results. The analyzed cloud parameters are thus only
rough estimates of the real clouds, but still serve as good indicators of the cloud conditions [Kokhanovsky et al., 2005]. Uncertainties may also be induced in the analysis due to the more long-lived accumulation-mode sea-salt aerosols, although the local wind seems to be in any case a good enough proxy for the lagrangian wind on the time scales considered for the accumulation and coarse mode aerosol particles (Nilsson et al., 2001). In addition, the difference in the spatial resolution in the MODIS and ECMWF data could also explain some of the variability that occurs in the present results.

The present results of the microphysical and optical properties as well as the estimated $N_d$ are planned to be evaluated based on model simulations. From this perspective, a process model will be developed, able to accurately handle both predictions of vertical mixing of water vapor and clouds as well as sea salt particles, for example according to a turbulent dynamical closure scheme (Glantz et al., 2004), and descriptions of gas-phase chemistry and aerosol cloud interactions (Mårtensson et al., 2010).

ACKNOWLEDGEMENTS

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INTRODUCTION

In these years we are observing an accelerating global temperature increase (IPCC, 2007). The temperature increase in the high Arctic has been particular severe with a double increase compared to the global mean (Hassol, 2004; Knepp et al., 2010). Furthermore, the Arctic receives long-range transported pollutants from sources located at mid latitudes, which together with the climate change stress the sensitive Arctic ecosystem (Quinn et al., 2011). Finally, the Arctic serves as a messenger for global change through clear signals as expressed by the ongoing melting of Arctic glaciers and sea ice and findings of pollutants emitted outside the Arctic. CO$_2$ is the most important greenhouse forcer but short lived species like O$_3$, methane and black carbon (BC) are together responsible for a temperature increase of the same order of magnitude (Quinn et al., 2008). Among those three climate forcers BC is expected to have the highest contribution through its absorbing characteristics in the atmosphere (direct aerosol effect) and its absorbing characteristics as deposited on snow. BC is one of the most important species in the high Arctic as the uncertainty related to its possible climate effects is very high.

METHODS

Station Nord (located at 81° 36' N; 16° 39' W, 25 m ASL) is a small military station operated by the Danish military and is manned year round by 5 soldiers. The department of Environmental Science at Aarhus University operates a monitor hut (Flygers Hut) 2 km outside the military camp at Drikkevandssøen. The site is thus very remote and only influenced very little by local pollution. Equivalent black carbon (BC) mass concentrations were measured by a particle soot absorption photometer (PSAP) operated at a wavelength of 550 nm between March 2008 and February 2011. Due to the low concentrations the measurements were averaged to daily mean values. Organic carbon and elemental carbon (OC/EC) were sampled by a high volume sampler (at ~ 0.5 m$^3$ min$^{-1}$) over 1 week from August 2008 to February 2011. The filters were analysed by an OC/EC analyser based on a thermal-optical method. The obtained values were used to calibrate the PSAP in order to obtain BC by derivation of the specific absorption coefficient. Furthermore, levoglucosan as a tracer for fresh biomass combustion was analysed from the same filters by LC-MSMS. The output from a hemispheric scale model was used to simulate BC concentrations at Station Nord. The model makes a polar stereographic projection, true at 60° north and with the North Pole in the centre. A spatial resolution of 150 km x 150 km, which can be nested to 50 km x 50 km was used. In this study, BC concentrations simulated with the Danish Eulerian Hemispheric Model (DEHM) (Christensen, 1997; Heidam et al., 2004) were compared to measured mass concentrations of BC at Station Nord. Finally, the BC mass concentrations together with a series of elements (Al, Fe, Cu, etc.) and inorganic ions (sulphate, nitrate etc.) obtained from a Filter Pack Sampler at Station Nord were analysed using the Constrained Physical Receptor Model (COPREM) to identify major sources (Wåhlin et al., 2003). Metals and inorganic ions were analyzed by IC (Ion Chromatography) or PIXE (Proton Induced X-ray Emission),
respectively. Source profiles used as input matrix for the model were based on a former study and combined with the newest results from the literature.

PRELIMINARY RESULTS

At Station Nord, a seasonal variation of the measured BC mass concentration is observed. This variation is in total agreement with observations of other air pollutants transported only during the polluted season (winter/spring) to the high Arctic. Based on the measurements with regard to the applied specific absorption coefficient, BC mass concentrations reach values up to 50 to 80 ng m\(^{-3}\) during the polluted season. In contrast, measured values are around 5 to 15 ng m\(^{-3}\) during the summer and autumn months. The general pattern of the BC mass concentration is reproduced qualitatively by the model results obtained by the Danish Eulerian Hemispheric Model (DEHM). But it has to be stated that the model underestimates BC mass concentrations in winter 2008 (see Figure 1) by a factor of two. During winter 2009, the model results are shifted compared to the measured data and the baseline during the summer months is in a general good agreement comparing model results and measurements.

![Figure 1: Comparison of measured and modelled BC mass concentrations at Station Nord. The measurements are based on a Particle Soot Absorption Photometer (PSAP) and the model results are based on the Danish Eulerian Hemispheric Model (DEHM).](image)

With regard to the source to receptor analysis, the COPREM model reveals that sulphur as well as BC mass concentrations are mainly originated from combustion processes and from emissions related to the metal industry located in Northern Siberia and Canada (see Figure 2). OC/EC relationships together with air mass back trajectory analysis indicate that during some periods biomass burning emissions significantly contributed to the observed pollutant concentrations at Station Nord. Nevertheless, this could not be proven by the COPREM results as the source profile of “Combustion” could not be split into “biomass combustion” and “fossil fuel combustion”, because relevant chemical markers for this split were missing.
Figure 2: Source contribution to sulphur and BC mass concentration based on source to receptor analysis at Station Nord using the CONstrained Physical REceptor Model (COPREM).

ACKNOWLEDGEMENTS

This work was carried out as part of CRAICC (Cryosphere-Atmosphere Interaction in a Changing Arctic Climate). The project was financial supported by The Danish Environmental Agency’s program on Arctic air pollution (Monitoring of short lived climate forcers in the Arctic).

REFERENCES


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 a dominant factor (Dusek et al. 2006) determining whether a particle is a potential cloud condensation nuclei (CCN), the 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 compositions (Swietlicki et al. 2008).

The aim of this study is to explore the hygroscopic and condensation nuclei properties of nucleation, Aitken and accumulation mode particles in sub- and supersaturation in a boreal forest (Hyytiälä, Hari and Kulmala, 2005) strongly affected by biogenic emissions from the forests during a period, which was exceptionally warm (summer 2010). The hygroscopicity parameters determined in sub- and supersaturations are compared with each other, and their information is coupled with the aerosol chemical composition data from aerosol mass spectrometer. During the measurement period, the measurement site was also affected by occasionally by forest fires in Russia and anthropogenic emissions from Tampere area (Williams et al. 2011). The effects of these variable aerosol sources to the hygroscopicity and CCN concentrations will be studied.

METHODS

This study was performed as a part of Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry (HUMPPA-COPEC-2010) intensive field campaign (Williams et al. 2011). The study was hosted in Station for Measuring Ecosystem-Atmosphere Relations II, SMEAR II, Hari and Kulmala, 2005) field station in Hyytiälä, Finland between 12 June and 12 August, 2010.

Hygroscopicity properties measurements were performed using a Hygroscopicity Volatility Tandem Differential Mobility Analyzer (HVT DMA, Hakala et al. 2010), while the CCN properties were measured with a commercial continuous-flow Cloud Condensation Nucleus Counter (CCNC, Roberts and Nenes, 2005). The instrument parameters and size range is presented in Table 1. In this study, the supersaturation of the CCN chamber is hold constant, while the diameter is scanned from 20 nm to 300nm with a Vienna-type Differential Mobility Analyzer (Winkmayr et al. 1991). The supersaturation is stepped from 0.2% to 1% before July 9th, and from 0.1% to 1% after that. For all data sets of supersaturation and activation diameters, derived from the CCN activation spectra, the effective hygroscopicity parameters κ were calculated from “κ-Köhler theory” equation (Petters and Kreidenweis, 2007) as follows:

$$ D_s = \frac{D^3 - D_d^3}{D^3 - D_a^3 (1 - \kappa)} \exp \left( \frac{4\sigma_{a/d} M_w}{RT \rho_a D} \right) $$

(1)
where $D$ is the droplet diameter, $D_d$ is the particle dry diameter, $\sigma_s$ is the droplet surface tension, which was approximated by that of water, $R$ is the gas constant, $T$ is the temperature, $M_w$ and $\rho_w$ are the molar mass and density of water, respectively.

By using the experimental activation diameter as $D_d$ and varying both $\kappa$ and the droplet diameter $D$, the $\kappa$ parameter can be iterated when the difference between the experimental supersaturation $S$ and the theoretical supersaturation $S(D)$ calculated from the Köhler curve of CCN activation (Eq. 1) reaches numerical minimum (Rose et al., 2010).

**Table 1. Instrument parameters during HUMPPA-COPEC 2010 intensive in Hyytiälä, Finland**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Description of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCNC</td>
<td>10 supersaturation levels were selected, particles were scanned from 20 nm to 300 nm</td>
</tr>
<tr>
<td>VHTDMA</td>
<td>RH=90%; Dp= 50, 75, 100, 110, 135, 150 nm; time resolution is around 3 min/dry size</td>
</tr>
</tbody>
</table>

**PRELIMINARY RESULTS**

Critical diameters corresponding to activation size in each supersaturation were calculated from the activation curve for each supersaturation along the time, which is shown in Figure 1. As expected, the critical diameter increased as the supersaturation decreased. Assuming a uniform composition, highest supersaturation leads to a lower activation diameter of the particles. As seen from the figure, at low supersaturation (<0.1%), the critical diameters had the largest variability. Some of this can be attributed to instruments uncertainty. The effective hygroscopicity parameters ($\kappa$), were plotted against time during July of 2010, see Figure 2. As a general trend, the hygroscopicity parameters ($\kappa$) increased as the supersaturation increased. In the other words, smaller particles had larger kappa values than the larger particles, which mean that the smaller particles were more hygroscopic than large particles. We have not yet implemented direct measurements of the chemical composition from Aerosol Mass Spectrometer, which need to be taken into account to verify these results. Further investigation of hygroscopic properties from HTDMA data will be analyzed in the following steps.

Critical diameters were also plotted against critical supersaturation in Fig. 3. The results obtained in this study agreed well with the previous study (Sihto et al. 2010) within the uncertainty. To further investigate the diurnal effect on critical diameter and kappa values, mean diurnal variation of critical diameters and kappa values at different supersaturation are also need to be presented. Figure 4 shows an example diurnal variation of critical diameters and kappa values at 0.1% supersaturation and 0.6% supersaturation.
Figure 1. Critical diameters for different supersaturation as a function of time during July of 2010 for boreal environment aerosols.

Figure 2. Hygroscopicity parameters obtained from CCN for different supersaturation as a function of time during July of 2010 for boreal environment aerosols.
Figure 3: Critical diameter as a function of critical supersaturation from this study and Sihto et al (2010).

Figure 4: Mean diurnal variation of critical diameter and $\kappa$ at 0.1% supersaturation.

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INTRODUCTION

Atmospheric particles have a strong impact on visibility and human health (Davidson et al., 2005; Nel, 2005). In addition, these particles have an effect on water circulation and earth’s radiative balance via cloud formation (Rosenfeld et al., 2008; Spracklen et al., 2008). Climate and health effects of atmospheric aerosols are determined by their properties such as their chemical composition. Aerosol chemical composition can be studied indirectly by measuring volatility of aerosol particles. Volatility measurements give also information on the properties of atmospheric semi-volatile organic compounds, which is important when modeling atmospheric partitioning between gas and particulate phases. The volatility of submicron aerosol particles (20 nm-1 µm) was studied in a boreal forest site at SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations II) station (Vesala et al., 1998; Kulmala et al., 2001) in Hyytiälä, Finland, during 01/2008-05/2010. The instrument used for the volatility measurements was VDMPS (Volatility Differential Mobility Particle Sizer), which consists of two separate instruments: DMPS (Differential Mobility Particle Sizer, Aalto et al., 2001) and TD (Thermodenuder, Wehner et al., 2002).

RESULTS AND DISCUSSION

AEROSOL VOLATILITY

Aerosol evaporation properties can be studied by heating aerosol at a certain temperature and comparing the total volume of aerosol particles before and after the heating. In the VDMPS system ambient aerosol sample was heated up to temperatures ranging from 80°C to 280°C. The higher the heating temperature was the more aerosol material was evaporated (Fig. 1). There was a non-volatile core present in aerosol particles even when heated up to 280°C. This result is in agreement with earlier studies in Hyytiälä (Wehner et al., 2005; Ehn et al., 2007). The observed non-volatile core explained on average (25±11)% of the total aerosol volume during 01/2008-05/2010. The volatility behavior of aerosol particles had a seasonal cycle. In winter and in autumn the fraction of non-volatile material in aerosol particles tended to be higher than in other seasons.

CONTRIBUTION OF BLACK CARBON TO THE NON-VOLATILE CORE

In order to study the chemical composition of the observed non-volatile core, the role of black carbon in the non-volatile residuals was determined. The mass concentration of black carbon was measured with Aethalometer (Hansen et al., 1982). On average 30% of the non-volatile volume was black carbon and thus, over a half of the non-volatile core volume was something else than black carbon. Black carbon could explain alone neither the composition of the non-volatile core nor the observed seasonal trend. According to Kalberer et al. (2004) some atmospheric organic species can form polymers that have very high evaporation temperatures.
CHEMICAL COMPOSITION AND SEASONAL BEHAVIOR OF THE NON-VOLATILE CORE

Meteorological data, air mass trajectories as well as aerosol mass composition measured directly with AMS (Aerosol Mass Spectrometer, Jayne et al., 2000) were analyzed in order to determine the properties of the non-volatile material (other than black carbon) in submicron particles. When air masses came to Hyytiälä from the clean sector (North-West), measured particle number concentrations and concentrations of gases such as carbon monoxide and sulfur dioxide were low. In that case the relative amount of non-volatile substance in aerosol particles was high. When air masses came from polluted areas (South-East) the relative amount of non-volatile material in aerosol particles was low but the absolute amount of non-volatile material was high. Interestingly, particles originating from the clean sector seem to include relatively more non-volatile residuals than particles arriving from polluted areas.

The AMS measurements were performed during spring and autumn 2008. Results from the aerosol mass spectrometry indicate indirectly that the non-volatile core consists of nitrate and organic compounds, especially during autumn time. It was seen that when air masses were clean both the fraction of non-volatile material in aerosol particles and the mass fraction of nitrate compounds in aerosol were high. During winter and spring time the non-volatile core (black carbon removed) correlated markedly with carbon monoxide (CO) concentrations as well as with sulfur dioxide (SO₂) and nitrogen oxide (NOₓ) concentrations. Due to this, it can be implied that the non-volatile core may also contain other pollutants in addition to black carbon. Thus, it seems that the amount of different compounds in submicron aerosol particles varies with season and due to that the chemical composition of the observed non-volatile core in these particles changes within a year.

Figure 1. Remaining aerosol volume after the heating process (Volume Fraction Remaining, VFR) as a function of thermodenuder’s temperature. The amount of data for temperature 280°C is the highest. Central mark in the box shows the median value of VFR. The upper edge of the box describes the 75th percentile of measurement points and the lower edge describes the 25th percentile, respectively. Whiskers are extended to the most extreme measurement points (5th percentile and 95th percentile) but they do not include outliers, which are presented individually with plus-marker.
ACKNOWLEDGEMENTS

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GAS PHASE SULFURIC ACID MEASUREMENTS WITH API-TOF-MS

TUIJA JOKINEN\(^1\), MIKKO SIPILÄ, HEIKKI JUNNINEN, TUUKKA PETÄJÄ, MARKKU KULMALA\(^1\) and DOUGLAS WORSNOP\(^{1,2,3,4}\).

\(^1\)Department of Physics, University of Helsinki, P.O.Box 64, Helsinki, Finland
\(^2\)University of Eastern Finland
\(^3\)Finnish Meteorological Institute
\(^4\)Aerodyne Ltd

Keywords: sulfuric acid, chemical ionization, mass spectrometry.

INTRODUCTION:

Sulfuric acid is a key compound in atmospheric nucleation (Sipilä et al., 2010). In atmosphere sulfuric acid is mainly produced photochemically, via reaction of OH radical and SO\(_2\). Sulfuric acid concentration in gas phase is typically very low, rarely exceeding 10\(^8\) molecules cm\(^{-3}\) (Paasonen et al., 2010). These very low concentrations set certain requirements for the detector to be used for quantitative measurements. In here we present a method to analyse gas phase sulfuric acid utilizing a highly selective ionization method first developed in 1993 by Eisele and Tanner (Eisele and Tanner, 1993). Aim is to deploy this new setup to measure ambient sulfuric acid and neutral clusters from the atmosphere.

METHODS:

Method for measuring gas phase sulfuric acid utilizing chemical ionization mass spectrometer (CIMS) was developed by Eisele and Tanner in 1993 (Eisele and Tanner, 1993). They used nitrate ion, NO\(_3^-\), and its clusters with nitric acid, HNO\(_3\), for highly selective chemical ionization of H\(_2\)SO\(_4\) via

\[
\text{NO}_3^-(\text{HNO}_3)_n + \text{H}_2\text{SO}_4 \rightarrow n \text{HNO}_3 + (\text{HNO}_3)_n\cdot\text{HSO}_4^-.
\]  

(R1)

Resulting (HNO\(_3\))\(_n\)·HSO\(_4^-\) clusters together with remaining NO\(_3^-\)·(HNO\(_3\))\(_n\), were dissociated and HSO\(_4^-\) and NO\(_3^-\) were detected with a quadrupole mass spectrometer. Here we present a measurement method in which the atmospheric pressure chemical ionization inlet, with geometry similar to Eisele and Tanner’s inlet setup (Eisele and Tanner, 1993) is coupled with a high resolution atmospheric pressure interface time-of-flight mass spectrometer, APi-TOF-MS (Tofwerk Ag.), (Junninen et al., 2010). In this present setup, clusters are not broken on purpose. Instead of braking clusters the high resolution and mass range of the TOF-MS allows separation and summing of several different clusters. Advantage of the method is that it allows one to seek for neutral sulfuric acid containing clusters formed by nucleation in the atmosphere (Kuang et al., 2008) or in laboratory systems (Sipilä et al., 2010).

In this laboratory experiment we generate reagent ions by mixing a small amount of nitric acid to nitrogen sheath flow and expose it to a radioactive source (\(^{241}\)Am) to form negative nitrate ions and nitric acid cluster ions. Sulfuric acid vapour is produced by leading synthetic air through a saturator containing pure liquid 95-97% H\(_2\)SO\(_4\). Sulfuric acid vapour is then introduced to the CI inlet with multiple different flow rates and diluted with laboratory air to create a constant sample flow of 10 lpm. The mixing with the reagent ions is done by applying voltage between a set of ion lenses.
The sample is guided to the TOF-MS section for mass per charge (m/Q) determination. In this section pressure is reduced to $10^{-6}$ mbar in three separately pumped chambers. Ions are guided to TOF-MS using two quadrupoles and an ion lens assembly. We operate TOF-MS in negative ion mode and use exact mass and isotopic patterns to identify and monitor sulfuric acid and its dimer, trimer and tetramer at mass to charge ratios (m/Q) 97, 195, 293, 391 and nitric acid monomer, dimer and trimer at m/Q 62, 125 and 188.

CONCLUSIONS

In this experiment it was clearly seen that deprotonated sulfuric acid concentration increases when flow rate through the saturator is elevated (Fig. 1). We increased the flow rate from 0.1 lpm to 9.5 lpm in constant steps. Using slow flow rates less than 1 lpm we can detect sulfuric acid monomer ($\text{HSO}_4^-$) and dimer ($\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$). When elevated flow rates (< 2 lpm) are being applied, we can also detect bigger clusters like sulfuric acid trimer ($\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$) and tetramer ($\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$). Nitric acid is been neutralized during ionization process which can be seen in descending signals of NO$_3^-$ and its dimer and trimer. Figure 1 shows increase in deprotonated sulfuric acid concentration when flow rate trough the saturator is elevated.

![Figure 1. Sulfuric acid and reagent ion concentrations in CI-TOF-MS spectrum.](image)

The aim of this experiment is to exploit CI-API-TOF-MS to measure aerosol clusters in ambient air and coupling chemical ionization with API-TOF-MS now offers an effective and highly selective way of ionizing and detecting ambient neutral sulfuric acid and its clusters.

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SEASONAL CYCLE AND MODAL STRUCTURE OF PARTICLE NUMBER SIZE DISTRIBUTIONS AT DOME C, ANTARCTICA

E. JÄRVINEN¹, A. VIRKKULA¹,², T. NIEMINEN¹, P.P. AALTO¹, E. ASMI², C. LANCONELLI³, M. BUSETTO³, A. LUPI³, R. SCHIOPPO⁴, V. VITALE³ AND M. KULMALA¹

¹University of Helsinki, Department of Physics, P.O Box 64, 00014 Univ. of Helsinki, Finland
²Finnish Meteorological Institute, P.O. Box 503, 00560 Helsinki, Finland
³Institute of Atmospheric Sciences and Climate of the Italian National Research Council (ISAC-CNR), Via Gobetti, 101, 40129 Bologna, Italy
⁴ENEA Area Sperimentale di Monte Aquilone, Manfredonia (FG), Italy

Keywords: Antarctica, Particle number size distributions, Dome C

INTRODUCTION

Antarctica is the cleanest continent and also the continent with least vegetation. A better understanding of Antarctic aerosols helps us to understand the influence of human activities on our climate. Aerosol number concentrations, size distributions and chemical composition have been studied at several stations around Antarctica. There exist long-term records of aerosol number concentrations, for instance from Neumayer (Weller et al., 2011) and South Pole (e.g., Samson, 1990) but aerosol number size distributions have been measured mainly during campaigns both at coastal stations (e.g., Ito, 1993; Koponen et al., 2003; Virkkula et al., 2007; Asmi et al., 2010; Pant et al., 2011) and in the upper plateau at South Pole (e.g., Park et al., 2004). The Norwegians recently started long-term size distribution measurements at the Troll station in Queen Maud Land (Hansen et al., 2009) but there are no long-term size distribution measurements from the upper plateau. The measurements presented here are the first step towards filling in this gap: particle number size distributions have been measured at the Dome C station (75°S, 123°E) in the upper plateau at about 3200 m amsl since December 2007. They were first stopped at the end of year 2009 due to technical problems but they were continued again in December 2010, and the goal is to continue these measurements. In this work we will present seasonal variation of the concentrations, the modal structure of particle number size distributions, and analyses of new particle formation episodes during the first continuous period until November 2009.

METHODS

Particle number size distributions in the size range 10-600 nm were measured with a differential mobility particle sizer (DMPS) that consisted of a Hauke-type medium-size DMA in a closed-loop arrangement and a TSI Model 3010 CPC. The time resolution of the raw data was 10 minutes. For this work hourly averages were used. Simultaneously with the aerosol measurements meteorological data were acquired. The wind data were used here to exclude data contaminated by the station itself.

Different modes were identified from the DMPS data with an automatic algorithm (Hussein et al. 2005). This algorithm parameterizes aerosol particle number size distributions with a multi log-normal distribution function. The multi log-normal distribution function is widely in use to parameterize the aerosol particle size distributions. The algorithm used was automatic and did not need a user decision for the initial input parameters. Only the maximum number of fitted modes was set to be three. It worked reducing the maximum number of possible modes with an overlapping test between adjacent modes.
RESULTS AND DISCUSSION

A clear seasonal cycle was seen from the number concentration data (Figure 1). The concentrations were at their lowest around July and August and at highest around January. In Figure 1 the short peaks in particle number concentrations are mainly contamination from the station. However, also natural new particle formation was observed. Particle formation events were rare and only happened in summer. Overall 13 events were observed during the measurement period. Event days are visible in the size distribution plot (upper panel of Figure 1) when the concentrations are red color coded.

The number concentration of different size classes (nucleation, Aitken, accumulation) differs from each other approximately by an order of magnitude. The highest concentrations were in the nucleation mode throughout the whole period, except in February 2009 and November 2009, when the highest concentration was in the Aitken mode. The lowest concentrations were usually in the accumulation mode. The concentrations in all the size classes followed the same seasonal cycle.

Figure 1. DMPS data from Dome C from 14 December 2007 to 15 November 2009. Upper panel: the size distribution of particles; middle panel: the total number concentration; lower panel: the concentration of the three size classes (nucleation mode: $D_p < 25$ nm; Aitken mode: $25 < D_p < 100$ nm; accumulation mode $D_p > 100$ nm).

To further visualize the differences in the size distributions in summer and winter, simple descriptive statistic was calculated, i.e., cumulative concentrations in each size channel of the data. The resulting size distributions show clearly that the modes of the size distributions are smaller in winter than in summer. In
winter the mode of the median size distribution was at about 20 nm and in summer at about 40 nm (Figure 2). It also shows that in summer concentrations were higher in every size class.

As explained above, the modal structure of the size distributions was studied by using the automatic mode-fitting algorithm. The number of modes as well as the mean diameter of them were calculated for every day during which there was data. The fitted three modes were the nucleation mode, the Aitken mode and the accumulation mode. Each day from one to three modes was able to explain the observed size distributions. When the concentration of particles was low (in winter), most of the time only one mode was present. When new particle formation took place or the air was more polluted, there were three modes. Figure 3 shows the relative frequency of the different modes that was calculated by summing up the occurrence of each of them and dividing this by the total number of size distributions in each month. The frequency of the nucleation mode was the highest from May to August when the total concentrations were the lowest. The Aitken mode was the most frequent in all other months but May to August when the
nucleation mode was dominant. The accumulation mode was significantly present in December and at the beginning of a year when nucleation occurred the most and particles were able to grow to bigger sizes.

Figure 3. Relative frequency of the occurrence of the three fitted modes in each month.

New particle formation events occurred in the Antarctic summer from November to March (Table 1). More than half of the observed events took place in early 2009. The formation rate, J, during the events varied from 0.004 cm$^3$/s to 0.28 cm$^3$/s and the median formation rate was 0.03 cm$^3$/s. The growth rate in size class 10-20 nm varied from 0.25 nm/h to 36.9 nm/h and the median growth rate was 1.59 nm/h.

Table 1. Formation rate, J, and growth rate, GR, for every particle formation event. First column: date of event; second column: formation rate and last column growth rate. The formation rate is the sum of the change in particle number concentration in size 10-600 nm (column 3), particle loss by coagulation (column 4) and particle loss by growth to larger size class (column 5).

<table>
<thead>
<tr>
<th>Day of an event</th>
<th>cm$^3$/s</th>
<th>cm$^3$/s</th>
<th>cm$^3$/s (10$^3$)</th>
<th>cm$^3$/s</th>
<th>nm/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J</td>
<td>dN/dt</td>
<td>Condensation growth</td>
<td>Coagulation</td>
<td></td>
</tr>
<tr>
<td>21.12.2007</td>
<td>0.283</td>
<td>0.102</td>
<td>1.438</td>
<td>0.179</td>
<td>36.917</td>
</tr>
<tr>
<td>10.1.2008</td>
<td>0.014</td>
<td>0.008</td>
<td>1.662</td>
<td>0.004</td>
<td>1.272</td>
</tr>
<tr>
<td>26.3.2008</td>
<td>0.017</td>
<td>0.016</td>
<td>0.136</td>
<td>0.002</td>
<td>0.247</td>
</tr>
<tr>
<td>9.11.2008</td>
<td>0.051</td>
<td>0.013</td>
<td>0.110</td>
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CONCLUSIONS

There was a clear seasonal cycle in the number concentrations, similar to that observed also at other Antarctic stations. However, this study is the first one that presents the seasonal cycle of the frequency of the main three modes of aerosol size distributions: the nucleation, the Aitken, and the accumulation mode. We have also analyzed new particle formation events. The median growth rate from 10 to 20 nm sizes in these events was 1.59 nm/h. Asmi et al. (2010) analyzed new particle formation events observed at the Finnish Antarctic station Aboa and found that the range of the growth rates was 1.3 – 2.5 nm h\(^{-1}\) in the same size range, from 10 to 20 nm. So, it seems there is not a very significant difference in the growth rates between these two sites. This is actually somewhat surprising, considering that Aboa is close to the ocean that is the source of most condensable compounds in the region and Dome C is high above the ocean and far away from the coast.

ACKNOWLEDGEMENTS

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DIFFERENCES BETWEEN LIGHT AND DARK CHEMISTRY ON CLOUD DROPLET ACTIVATION OF SALT AND DUST WITH SECONDARY ORGANIC MATTER

KESKINEN HELMI, JAATINEN ANTTI1, JOUTSENSAARI JORMA1, ROMAKKANIEMI SAMI1, MIETTINEN PASI1, AKI-MATTI KORTELAINEN1, LIGING HAO1, SMITH JAMES N.1,2 and LAAKSONEN ARI1,3

1Dept. of Applied Physics, University of Eastern Finland, P.O. Box 1627, 70211 Kuopio, Finland.
2National Centre for Atmospheric Research, 80307, Boulder, CO USA.
3Finnish Meteorological Institute, 00101, Helsinki, Finland.

Keywords: Cloud droplet activation, ammonium sulphate, desert dust, α-pinene

INTRODUCTION

Atmospheric particulate matter contains salt, dust and organic matter from natural sources such as oceans, dust-storms and forests. Understanding the influence of these components on aerosol-cloud interactions is vital for predicting their impacts on present and future climate (IPCC, 2007). This has recently activated several predictive laboratory measurements of particulate matter (Roberts and Nenes, 2005), e.g., cloud droplet activation by desert dust (Kumar et al., 2010) and salts with secondary organic matter (Smith et al., 2009).

Atmospheric salts such as ammonium sulphate (AS) is known to be very hygroscopic and act efficiently as cloud condensation nuclei (CCN). Inorganic mineral and dust particles are not as hygroscopic but they still have ability act as CCN (Herich et al., 2009, Kumar et al, 2009). A recent study by Kumar et al. 2010 focused on the CCN activity of fresh dust particles from multiple sources (e.g. Arizona and Sahara). Their major implication was that freshly-emitted dust and mineral aerosols could act as CCN through the effects of water adsorption alone. Actually, they showed that 100 nm dust particles can exhibit comparable hygroscopicity to that of organic species or a particle with AS volume fraction of 10%. Salt and dust atmospheric particles contain very often organics (Halquist et al., 2009). The secondary organic matter (SOM) itself, e.g., formed by α-pinene oxidation as is typical in pine tree forests, is also known to be quite hygroscopic (Saathof et al., 2003). Actually, this organic matter can heterogeneously coat atmospheric salt and dust particles and thus affect on their hygroscopic properties and cloud droplet activation. Recently, Smith et al 2011 studied the SOM coating affect on deliquescence and efflorescence of AS nanoparticles and found that it was only minuscule. On the other hand, the hygroscopicity of nanoscale soot agglomerates clearly increases with SOM coating up to the level of pure SOM (Saathof et al., 2003).

The aim of this study is to measure the affect of partitioning of secondary organic matter on the cloud droplet activity of salt and dust particles, with and without UV-radiation. The measurements were done in the Kuopio aerosol chamber. The AS and Arizona test dust (ATD) particles were coated by secondary organic matter produced by α-pinene ozonolysis. The cloud droplet activation measurements were made with a CCN counter.

METHODS

We used the Kuopio aerosol research chamber (Hao et al., 2011) to process the AS and ATD nanoparticles with secondary organic matter formed from α-pinene ozonolysis (Figure 1). The nanoparticles were generated from a salt solution or suspension using an atomizer (Model 3076, TSI Inc., USA). The AS (Sigma Aldrich, 99.999%) /water (de-ionized) solution concentration was set to 1 wt %. Solid content in the water suspension of ATD (0 - 3 µm, PTI, USA) was set to 0.1 wt %. The produced aerosol was fed to a diffusion drier (porous tube surrounded by silica gel) resulting relative humidity (RH) below 5 % (RH sensor, Rotronic).
The morphology of the ATD particles in the aqueous solution was studied by Transmission Electron Microscopy (TEM) (JEOL/ JEM 1200-EX). The TEM samples were collected on perforated carbon-copper grids (300 Mesh Cu, Agar, England) by depositing drops of a diluted suspension (0.005 wt%) directly on the grid for primary particle size image analysis and chemical composition analysis by energy dispersive spectroscopy (EDS).

Before each experiment the 6 m³ chamber was flushed and filled with pure filtered dry air. Secondly, the AS or ATD particles were introduced to the chamber and diluted achieving the desired concentration (~10⁴/cm³). Following this, during some of the experiments fluorescent UV-lights were turned on. In next step the 2 µl of α-pinene was injected to the chamber and, after 15 minutes of mixing, ozone was introduced to initiate oxidation. Ozone was generated by a UV lamp O₃ generator. Ozone enriched air (1.5 ppm) was introduced into the chamber (at 30 L/min) to achieve ozone concentration of 5 ppb. After that there was no flow into the chamber and chamber volume was slowly decreased by only the flow required by instruments (10.4 lpm). In all experiments, temperature was in the range of 25±2°C and RH in 5±2%, respectively.

During the experiment the particle size and concentration was monitored by scanning mobility particle sizer (SMPS) and condensation particle counter (CPC). Size-resolved CCN activity is carried out by using a differential mobility analyzer (DMA) parallel to the CCN counter. DMA was operated by stepping the voltage so that the dry particle diameters varied from 30 to 200 nm.

RESULTS AND DISSCUSSION

Figure 1 presents the morphology of the ATD nanoparticles. The ATD-nanoparticles shape varied from spheres to the clearly geometrical edged crystal shapes. This diverse morphology leads to the question of what shape factor we should use for these dust particles. The particle size measured by Image J from TEM-photos (Figure 1) was varying from 50 nm to 1 µm. Si, Al, Fe, Mg, Ca, Cr, Mn and Au were detected from the particles by elemental mapping. This corresponded quite well with the composition provided by the manufacturer: SiO₂, Al₂O₃, Fe₂O₃, Na₂O, CaO, MgO, TiO₂ and K₂O. However, in addition Cr, Mn and Au were clearly detected from several samples.

Figure 1. TEM micrographs from the ATD-nanoparticles, size, shape and composition of the dust particles is manifold. By Elemental mapping Si, Al, Fe, Ti, Mg, Ca, K, Cr, Mn and Au were detected.
Figure 2. Size distributions from pure AS and SOM-coated AS without (a) and with UV (b) radiation, and pure ATD and SOM coated ATD without (c) and with UV (d).

The measured size distributions before and after SOM coating with and without UV-irradiation are presented in Figure 2. After SOM coating of AS (Figure 2a) the small mode was observed. Thus, most probably new particles were also formed in addition to condensation onto existing AS seed particles. The concentration drop from uncoated to coated can explained by the dilution and wall losses over time. With the UV-light no new particle formation was observed (Figure 2b). However for the AS the SOM coating procedure was quite successful with and without UV-light. For the ATD clearly bimodal distributions were observed (Figure 2 c and d). The first mode with the mode diameter of 30 nm is most probably formed from water soluble fraction of the dust (including organics and salts) as we did not detect these particles with TEM (Figure 1). A similar bimodal distribution was observed by Gustavson et al. (2005). With SOM coating the particle number clearly increased and thus new SOM particles were formed. At the larger sizes, however, it appears that these primary particles have been coated by secondary organic matter.

Figure 3 Measured activation curves for AS (filled symbols) and SOM coated AS (open symbols) without (spheres) and without UV (triangles) at 0.5% supersaturation (SS) (a) and for ATD (filled) and SOM
coated ATD (open) without (spheres) and without UV (triangles) at 0.7% SS. Lines are presenting the sigmoidal fit for each activation curve.

Figure 3a shows the activation curves for pure and organic-coated AS with and without UV-light at 0.5% supersaturation (SS). The curves have a typical sigmoidal shape. The organic coating changed the AS dry activation diameter from 42 to 50 nm in dark and from 50 to 59 nm with UV-light, respectively. In fact, this small shift in activation diameter is expected and agreed well with other studies (e.g., King et al., 2007). The ~10 nm increase in activation diameter for organic-coated particles with UV-light is most probably caused by accelerated production of semivolatile compounds by UV radiation. For uncoated ATD we did not observed sigmoidal activation curves (Figure 3b, filled symbols). This is expected as they have strong variability in size dependent composition including soluble salts and organics and insoluble minerals from the natural ATD. However, the organic-coated particles had clear sigmoidal shaped activation curves. Again the UV-light shifted the dry activation diameter for coated particles from 57 to 69 nm at 0.7% SS.

Figure 4 Measured activation curves for AS at Dp = 60 nm (a) and ATD at Dp = 150 nm (b) with and without organic coating and UV light. Lines are presenting the sigmoidal fit for each activation curve.

In Figure 4a is presented the measured activation curves for the selected size Dp = 60 nm for AS with and without organic coating and UV light. The diameter is selected close to the particle maximum concentration (Figure 2a and b). The critical supersaturation (S_c) for pure AS in dark and with UV −light is now 0.3%. SOM coating increased the S_c to 0.39% in the dark and to 0.47% in UV light. For the dust particles the diameter of 150 nm was selected for the activation curve (Figure 4b) to represent the real pure and coated dust particles and not the soluble fraction or newly-formed new SOM particles (Figure 1 and 2 c and d). The SOM coating clearly decreased the S_c both in dark and in UV-light at least by factor 2. In fact, the S_c~0.2 at 150 nm for SOM coated dust is quite small and getting closer to the value observed for the pure SOM from α-pinene ozonolysis (Sc=0.15, King et al., 2007). UV-light did not have clear effect to the activation for pure or coated dust.

CONCLUSIONS

These preliminary experiments showed that for AS the organic coating from the ozonolysis products of α-pinene depressed cloud condensation activation. On the other hand, for the ATD particles the activity was enhanced by organic coating. UV-light inhibited the activation with increased organic coating for AS nanoparticles. These experiments will be further developed by supporting size-selective measurements of hygroscopicity, volatility and chemical composition from the experimental conditions presented here.

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ACKNOWLEDGEMENTS

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SPATIAL EXTENT OF NEW PARTICLE FORMATION EVENTS ESTIMATED FROM SIZE DISTRIBUTION AND TRAJECTORY DATA

N. KIVEKÄS¹, E. ASMI¹, M. KOMPPULA¹, A-P. HYVÄRINEN¹, J. LEPPÄ¹, A. VIRKKULA¹, Y. VIISANEN¹, P. AALTO², T. NIEMINEN², M. DAL MASO³, M. KULMALA³, B. SVENNINGSSON³, A. KRISTENSSON³, B. SVENNINGSSON³ A. ARNETH⁴ and H. LIHAVAINEN¹

¹Research and Development, Finnish Meteorological Institute, Helsinki, PO. Box 503, Finland
²Department of Physics, University of Helsinki, Helsinki, 00101, Finland
³Department of Nuclear Physics, Lund University, Lund, 223 62, Sweden
⁴Department of Physical Geography and Ecosystems Analysis, Lund University, Lund, 223 62, Sweden

Keywords: PARTICLE FORMATION, PARTICLE GROWTH, AMBIENT AEROSOL, DMPS

INTRODUCTION

Atmospheric new particle formation (NPF) has been observed all around the world (Kulmala et al., 2004). Usually the measurements have been carried out at a fixed location with instruments continuously measuring the air passing by. In these measurements the growth of the newly formed particle mode is often observed for several hours, even for several days after the particle production has ceased. This has led to an assumption that new particles are formed simultaneously over a large area, and as time passes by the particles observed later are those formed further and further from the station (Mäkelä et al., 1997; Kulmala et al., 1998). The extent of new particle formation events has been studied at vertical scale (Laaksonen et al., 2008), but not systematically in horizontal scale. In this study we present a method for analysing the horizontal extent of new particle formation in clean atmosphere, using only DMPS data and air mass trajectories.

METHODS

In a “Class I” (Dal Maso et al., 2005) atmospheric new particle formation (NPF) event the growth of the newly formed particle mode can often be followed for at least a couple of hours after the particle production has ceased (point A1 in Figure 1, hereafter referred as formation end time). At some point of time the growing mode disappears (B1 in Figure 1, hereafter referred as mode end time). If the NPF event is stable enough, the time difference between A1 and B1 (growth time) tells us how long time the particles formed at time A1 have grown before the mode can no longer be observed at the measurement site.

If we assume that the NPF event begins and ends over a large area simultaneously, and that there is not much horizontal mixing in the atmosphere, we can combine the growth time with trajectory data and locate the point where the air mass was when the formation of new particles ended and thus locate a point on the edge of the new particle formation area (NPF start location), marked with B2 in Figure 1.

This method has certain limitations and major uncertainties. It can be applied only to NPF events where the mode is observed to grow after the formation of new particles has ended. This rules out even part of the “class I” events, as well as all “class II” events.

The growing mode end time can be difficult to define due to instability or mixing of air masses, the new mode getting mixed with other particles or the mode being removed by some weather phenomena. Also the formation end time (A1) can sometimes be difficult to define in the DMPS measurement data. The
third source of major uncertainty is the trajectories, which can differ significantly from the actual route of the air parcel (Stohl and Siebert, 1998). The trajectory uncertainty in estimating the event start location (B2) is increased even more when the growing mode end time (B1) is uncertain.

![Diagram of a new particle formation event](image)

**Figure 1.** A schematic representation of a new particle formation event measured at a fixed location, showing the observed growth of the new mode in linear (left) and logarithmic (middle) particle size scales. The figure on the right shows the spatial extent of the event and the locations (A2 and B2) where the air mass was at times A1 and B1.

**TESTING THE METHOD**

To test the method we analysed more than 20 years of size distribution measurement data from stations Abisko, Pallas and Värriö in northern Scandinavia (Table 1). The stations are located in Sweden and Finland on an east-west line approximately 200 km apart from each other. All three stations represent clean background conditions with no major local particle sources. For each station eight FLEXTRA trajectories (Stohl *et al.*, 1995) for each day with 3-hour intervals were calculated for the whole measurement period, the end point being the station at 925 hPa pressure level.

<table>
<thead>
<tr>
<th>Station</th>
<th>Abisko</th>
<th>Pallas</th>
<th>Värriö</th>
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<tr>
<td>Longitude</td>
<td>19.05E</td>
<td>24.12E</td>
<td>29.58</td>
</tr>
<tr>
<td>Latitude</td>
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<td>67.97N</td>
<td>67.77</td>
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<tr>
<td>Altitude (m asl)</td>
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<td>565</td>
<td>390</td>
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<tr>
<td>Class I events</td>
<td>29</td>
<td>68</td>
<td>178</td>
</tr>
<tr>
<td>Analysable events</td>
<td>21</td>
<td>53</td>
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</table>

In the measurement data there were altogether 275 class I NPF events, of which 189 were analyzable with this method. In these events there were 23 events in which the air mass had passed over one of the other measurement stations during the growth period (A1 – B1) observed at another station, most often over Pallas on the way to Värriö. Among these events there were 13, where the data from both stations existed. For these cases the mode end times (B1) at Pallas station were calculated from the observed mode end times (B1) at Värriö, and from the time the air mass had spent moving from Pallas to Värriö. The calculated and directly observed mode end times at the Pallas station were compared, and a reasonably good agreement was found. In 12 of these 13 compared cases there was NPF observed at the Pallas station. In 9 of these cases the calculated and observed mode end times differed not more than 2 hours from each other. 2 out of the 3 remaining ones were cases where the event end time at Värriö was also uncertain. The event start locations (B2) were also compared in these cases, and the calculated and measured locations were mostly near each other, but not in all cases (Figure 2).

Based on the above we can say that the method works in general, but there are individual cases where the estimated event end location is incorrect. The method can be used as a statistical tool without major problems.
Figure 2. The new particle formation event end locations (B2) for the events passing over Pallas (red square) on the way to Värriö (cyan square). The red dots are the event end locations (B2) from data measured at Pallas and the cyan dots are those based on the growing mode end times (B1) calculated from Värriö data. The numbers are there to show which dots represent which event.

RESULTS

All 189 analysable events were analysed. The growing mode end time (B1) was uncertain in almost half of the events, because at some point the growing mode could not be followed any longer. Typically this was due to the mode mixing with other particle modes. In such cases the estimated event end location does not represent a point at the edge of the event area, but rather within the area.

The event start locations (B2) for all analysed events are shown in figure 3. Most of the event start locations were over land (figure 4), but there were some clearly over ocean as well. As the events with uncertain growing mode end time are included in the figures, the real event start locations are sometimes further from the stations than what the figures shows. Excluding the uncertain cases did not change the results systematically.

The starting and ending times of the new particle formation were found to be connected to the time of day and season. This was expected, since the NPF events have been observed to typically start when there is enough solar radiation available (Kulmala et al., 2004). The end time of the growing mode varied through the day without any clear correlation to time of day or solar radiation. This indicates that the boundary layer evolution is not affecting our results significantly.
Figure 3. The new particle formation event end locations (B2) for all analysed events. The larger black, red and blue dots mark the locations of Abisko, Pallas and Värriö measurement sites, respectively. The black squares, red triangles and smaller blue dots show the NPF event start location for the events observed at the station marked with the same color.

Figure 4. The growing mode duration (A1-B1) as function of the time the air mass had spent over land before arriving to the measurement site. The black squares, red triangles and smaller blue dots show the events observed at Abisko, Pallas and Värriö measurement stations, respectively.
CONCLUSIONS

A method for estimating the spatial extent of new particle formation (NPF) events has been presented and has been demonstrated to work in clean atmosphere. 189 new particle formation events from three subarctic measurement stations were analysed with the method.

The NPF start locations were typically not above ocean, which was seen in the comparison of growing mode duration and the time the trajectory had spent over land, as well as in mapping the NPF start locations. Also low correlation between the growing mode end times and time of day suggest that the growing mode end time is not determined by changes in solar radiation or boundary layer structure.

The ocean-continent boundary seems to be an important factor limiting the spatial extent of the new particle formation event. This is quite logical assuming that the air arriving from North Atlantic or Arctic Ocean contains only a few particles as well as very little condensable vapors. When the clean air arrives over land the vapor concentrations in the air start to increase. There is not enough pre-existing particle surface for the vapors to condense on, so new particles are formed. A large fraction of the new particle formation events started clearly inland, also on the supposedly clean west-to-north-east sector. This suggests that the ocean-continent boundary is not the only factor limiting the spatial extent of NPF events in the area. At least cloudiness and low amount of radiation available are assumed to hinder the new particles from forming.

The method will be tested more in near future. Also the events will be studied in more detail to estimate the effect of cloudiness and amount of radiation in the observed growing mode. The trajectory route before the onset of NPF will also be studied in order to see if the events starting over ocean can be attributed to continental plumes. Air masses passing over several stations during the event will also be studied more, because they provide us a measure of the real growth of particles in ambient conditions.

ACKNOWLEDGEMENTS

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CONCENTRATIONS OF SUB-2 NM PARTICLES IN SPRING 2011 AT THE SMEAR II STATION


1Department of Physics, University of Helsinki, Finland

Keywords: NANOPARTICLES, IONS, NUCLEATION, SULFURIC ACID

INTRODUCTION

Atmospheric new particle formation is proposed to happen via heterogeneous nucleation on molecules or clusters in the size range of 1-2 nm (Kulmala et al., 2000). These nanometer-sized condensation nuclei (nano-CN) can be either neutral or charged. The importance of ions in atmospheric new particle formation is still under discussion (Gagne et al., 2008; Yu and Turco, 2008) and also their fraction of the total nano-CN concentration is unclear. Recent field measurements have shown that in boreal forests there is a continuous pool of sub-3 nm particles and it seems to be dominated by neutral species (Kulmala et al., 2007; Lehtipalo et al., 2009). However, measurements especially in the 1–2 nm range are still needed to give more insight into the role of neutral and charged nano-CN in nucleation. In this work we present the first results from the measurements of sub-2 nm nano-CN conducted in spring 2011 at the SMEAR II station.

METHODS

Measurements were performed between March 14th and May 16th 2011 at the SMEAR II station in Hyytiälä, southern Finland. The total nano-CN concentration was measured with a particle size magnifier (PSM) which is a recently developed mixing-type condensation particle counter. PSM is able to detect particles down to the size of 1.1 nm (Vanhanen et al., 2011). Ions were measured by using the Air Ion Spectrometer (AIS; Mirme et al., 2007) and the Balanced Scanning Mobility Analyzer (BSMA; Tammet, 2006). The total nano-CN concentrations and ion concentrations were calculated from the measured data for four size classes ranging from 1.1 nm to 2.1 nm.

RESULTS

During the whole measurement period a continuous population of sub-2 nm nano-CN was observed. This population could be composed of small ions, their recombination products and other neutral species. Figure 1 presents the 1-hour average total nano-CN and ion concentrations in the size range of 1.3–1.6 nm during one week of the measurement period. From the figure it becomes obvious that the total nano-CN concentration exceeded clearly the concentration of ions during that week. It can also be noticed that the variation of the total concentration was stronger than the variation of the ion concentration.

The small concentration of ions compared to the total nano-CN concentration can also be observed when considering the median concentrations presented in the Table 1a for four size classes. In all size classes the median total concentration of nano-CN was significantly larger than the concentration of ions. In the size range of 1.3–1.6 nm, which is the most likely size range for nucleation to take place, the median total concentration of nano-CN was 959 cm⁻³ while the median concentration of ions was 250 cm⁻³. This indicates that on average 26% of the nano-CN population consisted of ions during the measurement period.
Figure 1. The 1-hour average total nano-CN and ion concentrations in the size range of 1.1–1.3 nm during one week of the measurement period. $N_{\text{tot}}$ is the total nano-CN concentration and $N_{\text{ions}}$ is the concentration of ions.

Table 1b shows the median concentrations of all nano-CN and ions during daytime on new particle formation days. During those time periods the median concentration of ions was $233 \text{ cm}^{-3}$ and the median total concentration of nano-CN was $1213 \text{ cm}^{-3}$ in the size range of 1.3–1.6 nm. Thus, the median concentration of all nano-CN was larger and the median concentration of ions was slightly smaller when comparing the data measured during new particle formation with all data. As a result also the median fraction of ions in that size range was then somewhat smaller. On average only 19 % of the total nano-CN concentration consisted of ions when studying only the data measured during new particle formation.

**CONCLUSIONS**

A continuous pool of nano-CN in the size range of 1–2 nm was observed in spring 2011 at the SMEAR II station. As the total concentration of this population was most of the time significantly larger than the measured ion concentration, the nano-CN population can't be explained solely by small ions. This proves that numerous neutral clusters had to be present at the site during the whole measurement period. The small fraction of ions during new particle formation also supports the earlier observations on the minor contribution of the ion-induced nucleation to the total particle formation in boreal forest conditions.

**ACKNOWLEDGEMENTS**

This work was supported by Cryosphere-Atmosphere Interactions in a Changing Arctic Climate (CRAICC), Finnish Centre of Excellence (FCoE) and Maj and Torr Nessling Foundation grant No 2010143.
Table 1. The median concentrations of ions and all nano-CN in different size classes a) during the whole measurement period b) during daytime on new particle formation days. \(N_{\text{ions}}\) is the concentration of ions and \(N_{\text{tot}}\) is the total nano-CN concentration.

<table>
<thead>
<tr>
<th>Size range (nm)</th>
<th>(N_{\text{ions}}) (cm(^{-3}))</th>
<th>(N_{\text{tot}}) (cm(^{-3}))</th>
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<td>1508</td>
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<tr>
<td>1.3–1.6</td>
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<td>959</td>
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<tr>
<td>1.6–1.8</td>
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<td>530</td>
</tr>
<tr>
<td>1.8–2.1</td>
<td>5</td>
<td>417</td>
</tr>
</tbody>
</table>

b) size range (nm) \(N_{\text{ions}}\) (cm\(^{-3}\)) \(N_{\text{tot}}\) (cm\(^{-3}\))

<table>
<thead>
<tr>
<th>Size range (nm)</th>
<th>(N_{\text{ions}}) (cm(^{-3}))</th>
<th>(N_{\text{tot}}) (cm(^{-3}))</th>
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<tbody>
<tr>
<td>1.1–1.3</td>
<td>358</td>
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<tr>
<td>1.3–1.6</td>
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<tr>
<td>1.8–2.1</td>
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REFERENCES


CHRYSOPHYTE STOMATOCYSTS – CREATING A TOOL TO RECONSTRUCT PAST ICE COVER TIMES AND SPRING TEMPERATURES IN FINLAND

S.T. KORKONEN\textsuperscript{1}, J.B. WECKSTRÖM\textsuperscript{1} and A.A. KORHOLA\textsuperscript{1}

\textsuperscript{1}Environmental Change Research Unit (ECRU), Department of Environmental Sciences, P.O. Box 65 FIN-00014 University of Helsinki, Finland.

Keywords: CHRYSOPHYTES, STOMATOCYSTS, ICE COVER, PALEOLIMNOLOGY

INTRODUCTION

Little is known about the past winter conditions and lake ice dynamics especially in the Northern region. Paleolimnology has proved to be useful when reconstructing past air and water temperatures when there is no recorded data available. The formation and melting of lake ice is largely controlled by air temperature. Latitude, altitude, lake morphometry and distance from the coast also play a key role in lake ice duration. Ice cover time and the length of the growing season affect among other things lake stratification, oxygenation, phytoplankton production, species composition and abundance.

This project aims to create a transfer function for chrysophyte resting stages (stomatocysts) in Finland to reconstruct past climatic conditions, especially past ice cover times and spring temperatures. Chrysophytes often dominate in the phytoplankton of oligotrophic alpine, arctic and subarctic lakes. Chrysophyte stomatocysts are considered to be good paleolimnological indicators because they are abundant and diverse in most Northern lakes, they preserve well in the sediment and many taxa have fairly well defined environmental optima and tolerances (Zeeb and Smol 2001). Chrysophytes distinct seasonality makes them suitable for creating seasonal inference models. At the moment most paleoclimatic reconstructions concentrate on past summer climatic conditions. This might leave changes happening during winter and spring undetected. Previous studies show that stomatocyst assemblages are related to the timing of the ice cover melting or the length of the ice cover period (Pla and Catalan 2005, Kamenik and Schmidt 2005b).

METHODS

Surface sediment samples were collected 2007-2008 from lakes around Finland using Limnos sediment corer. The sampled lakes cover different types of catchment areas from the northern barren treeless tundra to boreal forest and rural areas in the south. The lakes were chosen because of their known water chemistry and near neutral pH. Cyst sample preparation included treatments in H\textsubscript{2}O\textsubscript{2} and HCl to remove organic material and carbonates. Cyst types are identified from scanning electron microscope (SEM) images since some taxonomic features are too small to be resolved by light microscopy (Duff et al. 1995, Wilkinson et al. 2001). Unidentified cysts are classified using computer-aided SEM analysis (Kamenik and Schmidt 2005a). This approach has been successful when reconstructing winter/spring climate from Alpine lake sediments (Kamenik and Schmidt 2005b). The Finnish transfer function will be based on 62 subarctic lakes (half of them located north of the Arctic Circle), lake water chemistry and climatic data from nearby weather stations.
CONCLUSIONS

The new transfer function will be used to reconstruct spring temperatures for two Finnish lakes (Nautajärvi and Korttajärvi) with annually laminated (i.e. varved) sediments. The sediment in these two lakes is ideal for this purpose due to seasonal resolution (Ojala and Alenius 2005). The transfer function will also be used to compare pre-industrial and modern chrysophyte communities in 36 lakes located in NW Finnish Lapland to find out if cyst assemblages have been affected by anthropogenic stresses. It also has use in studies involving sudden environmental changes from one ecological state to another, ecosystem sensitivity, resilience and adaptive capacity to climatic and anthropogenic stresses. The results will bring new information to past lake ice dynamics and spring temperatures in the Northern regions.

ACKNOWLEDGEMENTS

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FIRST OBSERVATIONS OF MONOTERPENE ORGANOSULFATES IN WINTERTIME AEROSOLS IN DENMARK

K. KRISTENSEN, F. COZZI, A.M.K. HANSEN, M.F. LAURIDSEN and M. GLASIUS

Dep. of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Keywords: BIOGENIC SECONDARY ORGANIC AEROSOLS, MONOTERPENE OXIDATION PRODUCTS, CHEMICAL ANALYSIS

INTRODUCTION

Aerosols affect the radiation budget of the Earth by scattering of sunlight and affecting formation and lifetime of clouds. Oxidation products of biogenic volatile organic compounds, such as monoterpenes and isoprene, contribute to biogenic secondary organic aerosol (BSOA). The organosulfate derivatives of isoprene and monoterpenes, as well as their oxidation products, have been identified in both laboratory and field studies where they are formed through heterogeneous reactions involving sulphur compounds (e.g. Surratt et al., 2008), primarily emitted to the atmosphere from anthropogenic sources. Organosulfates of biogenic oxidation products thus provide a coupling between air pollution and formation of low-volatility BSOA, contributing to anthropogenically enhanced biogenic SOA (ABSOA) as suggested in recent studies (e.g. Hoyle et al., 2011).

Figure 1 Conceptual overview of formation of BSOA and ABSOA, and their climate effects.
METHODS

Particles (PM$_{2.5}$) were collected using a high-volume sampler at an urban background site in Aarhus, Denmark in January 2011. After extraction, the samples were analysed by HPLC coupled through an electrospray inlet to a quadrupole time-of-flight mass spectrometer (qTOF-MS) (Kristensen and Glasius, 2011). Organosulfates and nitrooxy organosulfates were identified from their characteristic MS-fragments (HSO$_4^-$, SO$_3^-$ and HNO$_3$) and the isotopic patterns of sulphur and nitrogen.

CONCLUSIONS

Two organosulfates of α-pinene and β-pinene were identified in the samples together with three nitrooxy organosulfates of monoterpenes (Table 1). All of these compounds have previously been observed in particle samples from Denmark during spring and summer (Kristensen and Glasius, 2011), as well as Norway, Sweden and Finland during summer (Yttri et al., 2011), but this is (to our knowledge) the first time that they have been identified in wintertime particle samples.

Table 1. Organosulfates identified in Danish PM$_{2.5}$ samples during winter (January 2011)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Suggested molecular structure</th>
<th>Molecular formula</th>
<th>Suggested precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organosulfate</td>
<td><img src="image" alt="Organosulfate structure" /></td>
<td>C$<em>{10}$H$</em>{15}$O$_5$S</td>
<td>α-pinene, β-pinene</td>
</tr>
<tr>
<td>MW 250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organosulfate</td>
<td><img src="image" alt="Organosulfate structure" /></td>
<td>C$<em>{10}$H$</em>{16}$O$_5$S</td>
<td>α-pinene, β-pinene</td>
</tr>
<tr>
<td>MW 280</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrooxy organosulfate</td>
<td><img src="image" alt="Nitroxy organosulfate structure" /></td>
<td>C$<em>{10}$H$</em>{17}$NO$_7$S</td>
<td>α-pinene, β-pinene</td>
</tr>
<tr>
<td>MW 295</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrooxy organosulfate</td>
<td><img src="image" alt="Nitroxy organosulfate structure" /></td>
<td>C$<em>{9}$H$</em>{15}$NO$_8$S</td>
<td>α-pinene</td>
</tr>
<tr>
<td>MW 297</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrooxy organosulfate</td>
<td><img src="image" alt="Nitroxy organosulfate structure" /></td>
<td>C$<em>{10}$H$</em>{18}$NO$_{10}$S</td>
<td>α-pinene, α-terpinene</td>
</tr>
<tr>
<td>MW 343</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Interestingly the level of organosulfates originating from isoprene was below the analytical detection limit in the wintertime samples, in contrast to a previous study in Denmark during spring (Kristensen and Glasius, 2011). This indicates that regional emissions of isoprene are very low at this time of the year.

The ground was snow-covered during the study period, so local emissions of monoterpenes are also expected to be minimal. The results thus point towards regional-scale processes affecting formation of ABSOA during winter, in accordance with the study by Frossard et al. (2011) in the Arctic.

ACKNOWLEDGEMENTS

We thank the VILLUM Foundation and the Nordic Top-level Research Initiative (CRAICC) for funding of this work.

REFERENCES


20 YEARS CLIMATOLOGY OF NO₃⁻ AND NH₄⁺ WET DEPOSITION AT NY-ÅLESUND, SVALBARD.

R. KÜHNEL¹, T.J. ROBERTS¹, M.P. BJÖRKMAN¹,2, W. AAS⁴, E. ISAKSSON¹, K. HOLMÉN¹ and J.STRÖM³

¹Norwegian Polar Institute, Fram Centre, N-9296 Tromsø, Norway.
²Faculty of mathematics and Natural Sciences, Oslo University, Postbox 1032, Blindern, N-0315 Oslo, Norway.
³Departement of Applied Environmental Science, Stockholm University, Svante-Arrhenius väg 8, SE-11418 Stockholm, Sweden.
⁴Norwegian Institute for Air Research, Postbox 100, N-2027 Kjeller, Norway.

Keywords: reactive nitrogen, ammonium, nitrate, precipitation, Arctic

INTRODUCTION

Human activities release reactive nitrogen such as NH₃ and NOₓ (NO + NO₂) to the atmosphere through energy production, fertilizer production and cultivation of crops (Galloway et al. 1995; Galloway et al. 2004; Grice et al. 2009; Peters et al. 2011). Nitrogen enriched air masses can be transported into remote, nutrient-limited regions, such as the Arctic, (Dickerson 1985) where the deposition of reactive nitrogen can significantly affect local ecosystems.

METHODS

This work presents a 20 years climatology of nitrate (NO₃⁻) and ammonium (NH₄⁺). It is based on a dataset of weekly precipitation observations by the Norwegian Institute for Air Research (NILU). Sampling of the chemical composition of precipitation have been performed by the Norwegian Institute for Air Research (NILU), facilitated logistically by the Norwegian Polar Institute (NPI), since 1980 in Ny-Ålesund on behalf of the Norwegian Climate and Pollution Agency (Aas et al. 2011). The deposited mass of nitrogen per m² through NO₃⁻ and NH₄⁺ was characterised, as part of the NSINK programme (http://nsinkproject.group.shef.ac.uk/NSINK/Home.html).

RESULTS AND DISCUSSION

A solid (16 September – 2 June) and liquid (3 June – 15 September) precipitation season was defined in accordance with the average form, in which precipitation occurred during the periods. The deposition samples were divided into the categories “weak” (< 2 mg N/m²) and “strong” (> 2 mg N/m²). Nitrate deposition occurred mainly during the solid season, whereas ammonium deposition occurred equally both in the solid and liquid season. Weak- and strong samples showed a ratio of occurrence of 9/1. However, the contribution to the deposited mass of nitrogen through weak- and strong samples had a ratio of 1/1. A strong interannual variability was observed due to strong samples.
Table 1 Mean annual number fraction of samples that deliver less or equal mass as threshold, and mass fraction of deposited nitrogen through these samples. The precipitation year (16 September – 15 September) was used for the calculations of the annual mean.

<table>
<thead>
<tr>
<th>Sample threshold</th>
<th>Number Fraction</th>
<th>Mass Fraction</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrate</td>
<td>Ammonium</td>
<td>Nitrate</td>
</tr>
<tr>
<td>0.5 mg N/m²</td>
<td>0.54</td>
<td>0.50</td>
<td>0.17</td>
</tr>
<tr>
<td>1 mg N/m²</td>
<td>0.78</td>
<td>0.72</td>
<td>0.39</td>
</tr>
<tr>
<td>2 mg N/m²</td>
<td>0.90</td>
<td>0.86</td>
<td>0.58</td>
</tr>
<tr>
<td>3 mg N/m²</td>
<td>0.93</td>
<td>0.90</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Figure 1: Annual budgets for nitrogen wet deposition through nitrate. Wide bars: Solid precipitation season; narrow bars: Liquid precipitation season.

The mean annual sum of total nitrogen deposition (nitrate + ammonium) was 74 mg N/(m² yr). Weak samples contribute an annual baseline of nitrogen deposition of approximately 17 mg N/(m² yr) that can be augmented by strong samples. Rapid and direct transport is likely the key factor for these strong samples.
Figure 2: Annual budgets for nitrogen wet deposition through ammonium. Wide bars: Solid precipitation season; narrow bars: Liquid precipitation season.

ACKNOWLEDGEMENTS

We would like to thank the Norwegian Institute for Air Research (NILU) and the Norwegian Meteorological Office (Met.no) for providing the precipitation data. We also would like to thank the Marie Curie Fellowship for funding the NSINK project. Additional funding came from CRAICC.

REFERENCES

EVIDENCE OF ANTARCTIC NEW PARTICLE FORMATION DUE TO CONTINENTAL BIOGENIC PRECURSORS

E.-M. KYRÖ1, A. VIRKKULA1,2, M. DAL MASO1, J. PARSHINTSEV3, J. RUIZ-JIMENEZ3, L. FORSSTRÖM4, H.M. MANNINEN1, P. HEINONEN5, M.-L. RIEKKOLA3 and M. KULMALA1

1 Department of Physics, University of Helsinki, P.O.Box 48, 00014 Helsinki, Finland
2 Air Quality Research, Finnish Meteorological Institute, P.O.Box 503, 00101 Helsinki, Finland
3 Department of Chemistry, University of Helsinki, P.O.Box 55, 00014 Helsinki, Finland
4 Department of Biological and Environmental Sciences, University of Helsinki, P.O.Box 65, 00014 Helsinki, Finland
5 Finnish Meteorological Institute, Finnish Antarctic Logistics, P.O.Box 503, 00101 Helsinki, Finland

Keywords: New particle formation, Secondary organic aerosols, Antarctic aerosols, Nostoc commune (Vaucher)

INTRODUCTION

Antarctica is the coldest, driest and cleanest of the continents. It is extremely isolated, especially during the winter, and has had no known sources of secondary aerosol particles on its surface (Ito, 1989) until present. However, during the Finnish Antarctic Research Program (FINNARP) 2009 expedition, the first evidence of Antarctic particle formation due to continental biogenic precursors was observed.

The Finnish Antarctic Research Station Aboa (73°03′S, 13°25′W) is build on a nunatak Basen, 500m a.s.l., some 130km from the open ocean. During the Antarctic summer, many meltwater ponds and trickles form to and around the nunataks (mountaintops) that are peaking out from the thick ice mass. These ponds hold a variety of biological activity in them (Jungblut et al., 2005), e.g. cyanobacteria Nostoc commune (Vaucher), a species very tolerant for extreme conditions (Dodds et al., 1995) and commonly found from Basen.

During the campaign, several aerosol and atmospheric composition measurements were carried out. The measurement devices were kept inside a small container, approximately 200m upwind from the main station. In addition to these measurements, samples of the cyanobacterial mat and water from the meltwater ponds were taken. The ponds were approximately 2.5km upwind from the container.

METHODS

The concentrations of neutral and charged particles as well as their size distribution and quartz filter samples were taken from the atmosphere, about 3 m above the ground level. The filters were changed three times a week. Different chemical compounds from the filter as well as water and Nostoc commune samples were analyzed later in Finland with a comprehensive two dimensional gas chromatography-time-of-flight mass spectrometry (GCxGC-TOF-MS). With this methodology, a great amount of different organic compounds can be detected. The neutral particle size distribution from 10 to 500nm was measured using a Differential Mobility Particle Sizer (DMPS, (Aalto et al.,
Air-Ion Spectrometer (AIS, (Hirsikko et al., 2005)) was used to measure the charged particle size distribution from 0.8 to 42 nm. The samples of water and Nostoc commune were kept frozen until they were analyzed.

Growth- and formation rates ($GR$ and $J$, respectively) were obtained for all new particle formation events from both charged and neutral particle size distributions. An additional estimation of apparent growth rates was applied to four apple- or bump-shaped events, where the traditional way of calculating the $GR$ was not feasible due to the shape of the event. HYSPLIT back-trajectories were calculated to estimate the origin of the nucleation and Aitken mode particles.

RESULTS AND DISCUSSION

During the campaign three periods of frequent new particle formation (NPF) and subsequent growth were observed. On contrary to the observations by Virkkula et al. (2009), most of the events were not associated with intrusion of air from upper troposphere. The $GR$ for the charged cluster ions as well as for neutral Aitken mode particles were high for Antarctica (Kulmala et al., 2004) and comparable to those measured over vegetated areas.

The most interesting period of NPF happened after the exposure of $N.\ \text{commune}$, from 1$^{st}$ to 3$^{rd}$ of January 2010. Unusually for Antarctica, the particle formation was very intense and almost continuous. The events started from the smallest cluster sizes and the particles grew very rapidly. In addition, the shape of the events was suggesting that the formation happened on a small scale, close to the station. To our knowledge, this has not been observed earlier in Antarctica.

Moreover, HYSPLIT back-trajectories were used to estimate the origin of the growing Aitken mode particles during the same period. The results showed that the particles had been born in the inland mountain ranges few hundreds of km’s away.

Even though the total surface area of the nunataks is quite small, they may be important source regions for secondary organic aerosols during the summer in Antarctica. In the future, as the climate warms, it is likely that more meltwater ponds will open up during the summertime and they will exist longer. This could increase both the aerosol number concentrations and their condensational growth and finally CCN and cloudiness. We hope, that our results will help in estimating the climatic feedbacks of aerosols and future climate in Antarctica.

ACKNOWLEDGEMENTS

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TRAINING AND KNOWLEDGE TRANSFER IN ATMOSPHERIC AND EARTH SYSTEM SCIENCE IN NORDIC COUNTRIES

A. LAURI\(^1\), J. BÄCK\(^2\), J. MALILA\(^3\), M. PARAMONOV\(^4\), T. VESALA\(^1\) and M. KULMALA\(^1\)

\(^1\)Department of Physics, P.O. Box 64, FI-00014, University of Helsinki, Finland
\(^2\)Department of Forest Sciences, P.O. Box 27, FI-00014, University of Helsinki, Finland
\(^3\)Department of Applied Physics, University of Eastern Finland, P.O. Box 1627, FI-70211, Kuopio, Finland
\(^4\)Finnish Meteorological Institute, Climate Change Unit, P.O. Box 503, FI-00101, Helsinki, Finland

BACKGROUND AND AIMS

Until the Top Research Initiative, the research and researcher training in the field of atmosphere-cryosphere-biosphere interactions was not coordinated. CRAICC will attempt to answer to the urgent need for an interdisciplinary program which would educate researchers to understand the complex interactions and processes governing the cryosphere formation and its influences on climate. Building a Nordic research network for studying associations between Arctic climate change, cryosphere, short-lived climate forcers and human activities requires expertise from a large number of research fields.

Despite the recognized need for multidisciplinary research on the topics covered by CRAICC, undergraduate students are typically educated within their specific disciplines without much multidisciplinary aspects, which however provide a strong scientific basis. At PhD and post-doctoral level, the shift from discipline-tied fundamental education towards multidisciplinarity is imperative for a successful career in climate and global change science. Therefore, the chief educational and knowledge transfer goal is to educate a next generation of scientists in a truly multidisciplinary way of thinking. Within CRAICC, researcher training will be done through interdisciplinary intensive field courses and summer and winter schools gathering students from all Nordic and Baltic countries as well as the whole Arctic area to work together in a multidisciplinary scientific context.

TRAINING PROGRAMMES

Within CRAICC, education and knowledge transfer have been given a special emphasis. Following the CBACCI Education Structure (CBACCI, 2003), determined work has been carried out to develop the multidisciplinary training on all levels (master students, doctoral students, postdoctoral scientists, professors). The following training programmes have been initiated:

- Nordic Master’s Degree Programme in Atmosphere-Biosphere Studies: started in 2006, coordinated by University of Helsinki, 10 university partners in Finland, Sweden, Denmark and Estonia
- Nordic Graduate School CBACCI (Biosphere-Carbon-Aerosol-Cloud-Climate Interactions): started in 2003, coordinated by University of Helsinki, 14 partners (10 universities, 4 research institutes)
- National Graduate Schools
- Marie Curie Initial Training Networks

CRAICC will serve as an additional component in the existing programmes. CRAICC has also established a Nordic staff exchange scheme, which is available also for research students.

ACTIVITIES WITHIN THE PROGRAMMES

Within CRAICC the specific training activities include:

- multidisciplinary research training courses;
- inter-university and -institute supervision;
- student, teacher and senior scientist mobility;
- students’ participation in international conferences, symposia and workshops;
- teacher workshops;
- use and development of new education technologies;
- training in transferable skills.

Research training courses are typically organized jointly, either as a one- or two-week intensive courses, usually in one of the measurement stations, or as e-learning. The training on the intensive courses includes scientific and technological knowledge, transferable skills and public outreach. These courses combine core and transferable skills, always ensuring that these skills are learned actively and kept fully relevant to the students’ own research. The topics of these courses includes e.g. data analysis, model-data assimilation, formation and growth of atmospheric aerosols, Arctic air pollution, cloud microphysics, and atmosphere-biosphere exchange. The transferable skills included in the education have included working in the field, atmospheric instrument technology, data analysis, computer modelling, writing articles, presentation skills, project management, writing proposals, and commercialization of scientific ideas.

The intensive courses are available both for master and doctoral students, and combine several CRAICC work packages each. The courses offer the participants hands-on teaching in specific topics, as well as excellent opportunities for exchanging knowledge and interacting with more experienced researchers in multi-disciplinary arena. The training is a combination of theoretical lectures, field measurements, computer modelling and complementary skills. Training on transferable skills is usually given by internationally acknowledged and inspiring visiting researchers.

CRAICC will organize intensive field courses several times a year. These courses are aimed to be of great interest to both students and researchers. The forms of working during intensive courses include lectures, exercise sessions, seminars, discussion sessions, field work as well as social activities. Very often the emphasis is placed on intensive work in small student groups. From the pedagogical point of view, the intensive courses often represent a form of problem-based learning (PBL; see e.g. Duch et al., 2001). This instructional strategy was adopted in order to emphasize the students’ own responsibility of their learning process, with support from the instructor. The goals for the course are often set by the students in the beginning of the course, after a few introductory lectures. Teachers take the role of facilitators rather than lecturers. Collaborative learning is carried out throughout the courses. This allows for the social construction, sharing of information and cognition, and finally improves the metacognitive skills of the students which, in turn, enhance self-directed learning skills. We have also noted that motivation and sociability is blossoming in these small groups, which allows the students to easily adopt the studied issues and open their minds for creative problem-solving.

On the senior scientist level, workshops for teachers and supervisors have been held annually in the context of CBACCI. The two-day workshop includes two parts: training for teachers and discussions educational co-operation and education development. The participating lecturers and supervisors are trained on teaching, communication and supervising skills, including web-based teaching.

Concerning education and knowledge transfer, special attention has been paid to the transfer of good practices. The joint events, especially the annual workshop for teachers and supervisors, include discussions and evaluation of the practices of the partners.

**NEW TECHNOLOGY TO SUPPORT TEACHING**

An example of the new technology used in the research-oriented joint programmes at the University of Helsinki is Smart-SMEAR, a tool for structuring, visualising and analysing complex environmental field data (Junninen et al., 2009). Smart-SMEAR is a handy and inspiring tool to present complex environmental measurement data, and to see different causal connections in an understandable and simple way. The tool consists of two separate applications. The first is a visual implementation of the 15-year continuous dataset from the SMEAR II environmental and atmospheric measurement station in Hyytiälä, Finland (Hari and Kulmala, 2005), and the second one is used to download the desired data for further
The central pedagogical idea is student’s inspiration through getting the idea. The Smart-SMEAR database contains several measured and modelled parameters, each of which requires special tools and knowledge to work with. The web-based tool collects and processes all the data so that the user does not have to know practically anything about how the data should be treated. This provides means for beginning scientists, students and researchers from other fields to explore the data and see correlations and behaviour of different parameters without losing time in collecting data, pre-treatment and learning special plotting tools (e.g. plotting maps and surface plots).

The pedagogical philosophy of the Smart-SMEAR is based on the idea of meaningful learning. Smart-SMEAR emphasises learning as the learner’s own process of constructing new information on top of the already achieved knowledge. This poses a few requirements to the learning environment. First, the already existing information structures and understanding of the student must be correct and well organised, so that the learning of the new information becomes meaningful. This can be achieved via various methods: discussions in small groups, questions, simple recapitulation and outliners. Second, the teaching becomes coaching, where the teacher allows the student to create understandable and meaningful information structures out of the material to be studied. This presumes that various pedagogical approaches are adopted, e.g. collaborative learning, reading and writing, discussions. The activity and motivation of the students play the key role. Third, the students need to have the time and space for reflection, which means that the students can evaluate their own learning and develop their metacognitive skills. This way they have the possibility to become experts of their own learning process. Fourth, the Smart-SMEAR emphasis on social interaction and shared cognition. It has been shown that working in small groups and talking about the cognitions enhances understanding (Hennessy & Murphy, 1999). Social interaction can consist e.g. of internet-discussions and reading and commenting each other’s texts.

The contextuality and constructiveness of Smart-SMEAR are based on the idea that by associating old and new knowledge in a meaningful way the student achieves true expert information, which is thoroughly understood and, thus, correct and reusable. The experiences have shown that students with very different backgrounds benefit from the usage of Smart-SMEAR. The tool was used as a part of teaching first time on an intensive field course given in spring 2007, and it was admitted an honourable mention in the University of Helsinki educational technology competition in 2007.

REFERENCES

PARTICLE SIZE MAGNIFIER AS A TOOL TO DETECT ATMOSPHERIC AEROSOL PARTICLES, IONS AND CLUSTERS SMALLER THAN 2 NM

K. LEHTIPALO1,2, J. KONTKANEN1, J. KANGASLUOMA1, J. VANHANEN2, J. MIKKILÄ1,2, H.E. MANNINEN1, M. SIPILÄ1, T. PETÄJÄ1 and M. KULMALA1

1Department of Physics, University of Helsinki, 00560 Helsinki, FINLAND
2Airmodus Oy, 00560 Helsinki, FINLAND

Keywords: nucleation, CPC, nano-particles, field measurements.

INTRODUCTION

The studying of new particle formation was long limited by the inability to detect neutral particles smaller than about 3 nm, which is the size range where nucleation happens. Sipilä et al. (2008) showed the applicability of condensation particle counters to measure in the sub-3 nm range also in field conditions. Since it cannot be resolved by CPC measurements only if the activated seed-particles are large molecules, clusters, or actual particles, it has become customary to call them nano condensation nuclei (nano-CN). Nano-CN are always present in the boreal forest boundary layer, even when no particle formation is detected with traditional instrumentation (Kulmala et al., 2007; Lehtipalo et al., 2009). However, there is still controversy about the role of nano-CN and ions in new particle formation, as well as how much ions contribute to the total nano-CN concentrations (Yu and Turco, 2011).

METHODS

Measurements were conducted in the boreal forest region at the Hyytiälä SMEAR II station in Finland as a part of HUMPPA-COPEC campaign in late summer 2010, and also during spring 2011. The Airmodus A09 Particle Size Magnifier (PSM) was used to resolve the size distribution of particles below 2 nm. The PSM is a dual-stage mixing type CPC using diethylene glycol for activating and initial growth of particles, while further growth and counting is done by an external CPC. The cut-off size of the instruments can be varied between about 1-2 nm by altering the mixing ratio of saturator and aerosol flow and thus changing the supersaturation created. The relation between the mixing ratio and activation diameter has been determined in laboratory calibrations using mobility standards and size-selected tungsten oxide and silver ions. The nominal cut-off size of the Particle Size Magnifier at the highest mixing ratio is about 1.5 nm (Vanhanen et al. 2011).

 Additionally, the particle size distribution between 3-1000 nm was measured with a twin-DMPS, and the ion mobility distribution with a Balanced Scanning Mobility Analyzer (0.8-7.5 nm; BSMA; Tammet 2006) and a Neutral cluster and Air Ion Spectrometer (0.8-40 nm; NAIS; Mirme et al., 2010). The composition of ambient ions was measured with an API-TOF mass spectrometer (Junninen et al. 2010). We deployed also an ion-DMPS consisting of a TSI nano-DMA, a pulse-height CPC (Sipilä et al., 2010) and a switchable neutralizer, which alternately measures the positive and negative ion and the neutralized size distribution down to about 2 nm.

CONCLUSIONS

We found the Airmodus A09 PSM well suited for long-term field measurements, and the concentrations of nano-CN were in agreement with previous studies using pulse-height CPC (Lehtipalo et al. 2009). Figure
1 shows an example day with total particle concentrations measured with PSM at cut-off sizes 1 and 2 nm, and for comparison a ultrafine CPC (TSI 3776) with cut-off at 3 nm. During daytime, the PSM showed higher concentrations compared to the ultrafine CPC, while the concentration of small ions remained almost constant. This indicates the presence of neutral nano-CN between 1-2 nm during that time.

We observed that the fraction of ions from all particles in the size range between 1-2 nm was diminishing with increasing total concentration. Generally, the total nano-CN concentration varied much more than the small ion concentration. Correlation was also found between the concentration of sulphuric acid (as measured with a chemical ionization mass spectrometer) and the concentration of nano-CN.

Figure 1. Example of total particle concentrations in Hyytiälä on 31.3.2011 measured with the PSM at cut-off sizes ~1 nm and 2 nm, compared to TSI 3776 ultrafine-CPC at 3 nm cut-off size.

ACKNOWLEDGEMENTS

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PARTICLE ANALYSIS OF VOLCANIC ASH WITH ELECTRON MICROSCOPY

K. I. LIEKE¹, T. B. KRISTENSEN¹, K. B. KOCH², M. BILDE¹, S. LEDERER³

¹Copenhagen Center for Atmospheric Research, Department of Chemistry, University of Copenhagen, 2100 Copenhagen, Denmark.

²Faculty of Life Sciences, University of Copenhagen, 2300 Copenhagen, Denmark.

³Department of Materials and Geosciences, Darmstadt University of Technology, 64287 Darmstadt, Germany.

Keywords: Volcanic Ash, Electron Microscopy, Mineralogy, Melting.

INTRODUCTION

Since the Airspace closure over Europe due to the Eyjafjalla eruption in 2010, volcanic ash came more in the focus of atmospheric science. Many remote sensing studies and models tracking the Eyjafjalla ash plume were published within the last year (Ansmann et al. 2010, Langmann et al. 2011, and others). But the inconsistent behaviour of authorities of many European countries regarding the airspace closure after the Grimsvötn eruption in this year clearly stated that the properties and impacts of volcanic ash particles are still not fully understood. Ash particles are reported to cause damage to jet engines (Grindle and Burcham 2003), which may result in engine failure, and damage to aircraft windows by sandblasting through their hardness and density and thereby decrease visibility. Volcanic ash plumes may cover the sky in layers for days or weeks and thus have climatic influence by direct effects, but due to the unknown mineralogical composition it is hard to assess an ash plumes bulk refractive index. The ice nucleation abilities of volcanic ash particles are observed (e.g. Durant et al. 2008).

After the Eyjafjalla eruption many conference contributors presented volcanic ash particles from different sites and observed with numerous methods, but failed to distinguish them from the background and describe their characteristics which separate volcanic ash from mineral dust as for example Saharan dust, which is also frequently transported over Europe.

We collected particles before and after the Grimsvötn volcanic ash arrived Copenhagen, Denmark between 23 May and 31 May 2011. We compare the results to analyses of different volcanic ash samples of the Eyjafjalla eruption in April 2010. We also conducted melting experiments on single ash particles and report structural characteristics. The chemical composition is compared to Saharan mineral dust, showing a different mineralogical signature. We are able to present unique data about single particle chemical composition, size and morphology and thus some characteristics of volcanic ash particles.

METHODS

Single particle analysis was performed using an ESEM Quanta 200 FEG, FEI (Eindhoven, The Netherlands) equipped with a microanalysis unit for energy dispersive X-ray detection of single particles. A post processing of data was conducted according to the scheme described and used in Kandler et al. (2011) which sorts particles in groups according to their elemental composition. Only particles with diameters larger than approximately 1 µm average diameter were taken into account for analysis. Secondary electron images and corresponding spectra were recorded prior to and after melting particles in a tube furnace in certain temperature steps between 800 and 1100 °C.

The (assumed) mineralogical composition of particles was compared using an element index which is defined as the atomic ratio of an elements considered and the sum of all elements from sodium to iron.

Table 1 lists all analysed samples. The Copenhagen clear day reference and volcanic ash samples were collected on adhesive carbon substrate for use in electron microscopy. The Iceland ash collected from the ground in the vicinity of the Eyjafjalla was sieved and brought on polished Platinum disks for analysis.
Tab. 1 Table of samples and related sampling times

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Start</th>
<th>Stop</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear day reference</td>
<td>University of Copenhagen roof top</td>
<td>23 May 18:50h</td>
<td>24 May 12:28h</td>
<td>Dry + wet deposition</td>
</tr>
<tr>
<td>Transported volcanic ash</td>
<td>University of Copenhagen roof top</td>
<td>24 May 12:35h</td>
<td>30 May 09:30h</td>
<td>Dry + wet deposition</td>
</tr>
<tr>
<td>Iceland ash</td>
<td>Eyjafjalla Volcano, within 50 m radius of the crater</td>
<td>April 2010</td>
<td></td>
<td>Deposited fall out upper most layer</td>
</tr>
</tbody>
</table>

Figure 1 secondary electron images and EDS spectra of selected particles of the Copenhagen volcanic ash sample

RESULTS

A characteristic chemical composition, as shown exemplarily in the two spectra of Figure 1 was found to be indicative for volcanic ash. In the clear day reference sample which is not influenced by the eruption, quartz (or other SiO$_2$-phases) is the most abundant particle group with 45 % relative abundance (Figure 2) followed by the group of Si-Al (Al$_2$SiO$_5$) particles representing some clay mineral phases. Feldspars, mostly represented by the groups SiAlK (Potassium feldspar), SiAlCa+Na (Plagioclase) were abundant but below 10 %. The group of other Si-dominated particles, which usually represents mixtures of silicates (Lieke et al. 2011) was mainly composed of Al-Si particles containing iron and other trace elements (e.g. Na, Mg, Ca, K) to some extend, only two particles were found containing titanium additionally. The Copenhagen volcanic ash sample contains basically the same particle groups, but with varying abundances (Figure 2). Quartz (or other SiO$_2$-phases) and Si-Al are reduced to 20 % relative abundance, whereas the Feldspar-groups are relatively increased, foremost SiAlNa (representing e.g. Albit) to almost 10 % abundance. The group of “other Si-dominated” shows higher relative abundance due to the presence of particles containing Na, Mg, Ca, Ti, Fe, and Al:Si of almost 3 (see also Figure 1). In total, 15 % of the analysed particles show this typical composition,
which was regarded as indicator for possible volcanic origin. Many of them contain high amounts of Ca. In the reference sample, less than 1 % of the particles were of similar composition. Furthermore, Fe and Mg containing silicate groups (probably amphibole, pyroxene, olivine) are more frequently occurring, also containing particles with minor amounts of Ti (which possibly could be allocated to volcanic origin as well).

Figure 2 diagram of relative number abundance of particle groups for two different samples, n is the number of analysed particles. The columns display a comparison of silicate containing groups for the clear day reference sample and the Copenhagen volcanic ash sample.

The sieved particles of the Iceland ash (Eyjafjalla) consist of particles which could be identified as feldspars, but the majority of particles displayed a composition similar to that shown in Figure 1. Particles started melting soon above 900 °C and the majority of particles was completely melted below 1000 °C. Pictures of the material after tempering of 1000 °C show clearly melted droplet-like particles, but partly crystallising fragments on the actual particles surface. Calorimetric measurements of the bulk material pointed to a partly crystalline composition of the sample with the plagioclase phase melting at 1340 °C. The majority of particles is melting below 1000 °C and showing typical behaviour of glass in the melting curve. The elemental composition of particles didn’t change.

The Copenhagen volcanic ash sample particles have an average aspect ratio of 1.9 (Median 1.76) and the reference sample particles display an even lower value of 1.8 (Median 1.65). Many of the particles associated with volcanic ash appeared triangular or half-rounded presenting some sharp, fractionated edges in the electron images.

The volcanic ash related particles of the Copenhagen sample have a Si/Al atomic ratio of 2.8 (2.96 Median) in average. This is consistent with aircraft observations by Schumann et al. (2010) of the Eyjafjalla ash cloud in 2010 of 17 May, reflecting a larger contribution of feldspar minerals. In comparison, the iron content is slightly lower, 0.26 (Median 0.25), than the value of 0.33 observed by Schumann et al. (2010), which might be due to the difference of the regarded size intervals between this study and the aircraft observations closer to the source. The average Ti/Si ratio in the present samples (transported volcanic ash particles) is 0.05 (Median 0.04), for all investigated particles of the Eyjafjalla sample, Ti was below the detection limit.

The contribution of volcanic ash particles to the background aerosol over Copenhagen in May 2011 gets very clear when plotting the silicate particles in a ternary diagram with the axes displaying the typical elemental composition of feldspars and clay minerals. The volcanic ash particles are mainly plotting in a bulky cloud in the centre of the diagram in Figure 3, right side. Those particles are completely absent in the clear day reference sample, as shown in Figure 3, left side. This indicates a clear change in particles chemical composition in presence of the ash cloud over Copenhagen from 25 May on.
The composition of the particles displayed in Figure 3 doesn’t match any common mineral phase. This also leads to the conclusion that they are volcanic glasses. The most common mineral phases plot along the axes. Like shown in Lieke et al. (2011), the mineral mixtures which can be found in Saharan mineral dust display in the upper region of the diagram. Overlaying of all data (not shown here) shows clearly a different chemical signature for transported volcanic ash and Saharan dust. The atomic ratios are consistent with those of aircraft observations reported by Schumann et al. (2010) of the Eyjafjalla ash cloud in 2010, when the Falcon aircraft flew into the plume to sample volcanic ash particles. The composition of volcanic ash particles and glass depends of course on the composition of the magma and on the type of eruption; therefore it is not easy to compare the results presented here to other studies of airborne volcanic ash. The composition of Eyjafjalla and Grimsvötn should be different. Unlike Eyjafjalla, which erupts silicic magma, Grimsvötn characteristically erupts basaltic magma (Oladottir et al. 2011). Basaltic magma is generally composed of amphibole, pyroxene, plagioclase, feldspars and olivine. Most of the phases (determined only from chemical composition) are found in the presented samples collected over Copenhagen. However, the glass like particles show a composition which is so far not reported in other studies.

Horwell et al. (2003) describe glass enrichment in the finer fractions and plagioclase enrichment in the coarser fractions for samples from Montserrat, but the particles considered to be volcanic glass show a different composition than the Iceland-volcanic ash particles considered in this study. The British Geological Survey (Loughlin, 2011) reports sharp, angular glass shards, flat and platy glass with smaller particles stuck to the surface and aggregates of these with diameters between 1 and 50 μm, from ash falls over UK. Loughlin (2011) suggests that this variety of textures was formed as the magma was erupted while being fragmented rapidly into tiny pieces by two types of explosion: very rapid bubble growth caused by decompression of the rising magma and by interaction with water, leading to a steam caused explosion. The particles collected over Copenhagen reflect some of the forms reported by the British Geological Survey but is, probably due to longer transport times, more fragmented and agglomerated.

From a mineralogical point of view the melting experiments of the Iceland ash revealed a multi-phase system of glass and minerals for the bulk material (powder). Complex particle structures were found in the electron images. Estimations of single particle physical properties like density and refractive index are thus a yet not possible to make. However, a melting range of 900 to 1000 °C for the majority of particles could be estimated. This range refers to particles with a chemical composition as shown in Figure 1 and as found in both, Eyjafjalla and Grimsvötn samples. To determine the exact melting point (or at least a more narrow range) the experiments should be repeated, applying in situ heating experiments in an Environmental Electron Microscope. The same could be applied setting particles to an undercooled atmosphere, to investigate their actual ice nucleation ability.

To further discuss the hazard of ash to aircraft engines, it would be advantageous to perform test rig studies with an commercial aircraft turbine and volcanic ash from different sources. Thus a critical concentration for different volcanic ash types and mineral dust could be determined.

![Figure 3 ternary plot of volcanic ash particles (left) and the clear day reference sample including typical elements of feldspars and clay minerals (axes)](image)
ACKNOWLEDGEMENTS

This work was arising out of occasion and thus not financially supported by any Research Council or other Organisation. Without the will and technical support of many people within the aerosol community and related fields, we would not have been able to conduct the presented experiments. First and foremost, we thank Claudia Fasel at the Technische Universität Darmstadt for conducting calorimetric measurements. The melting behaviour of the particles was observed in a student practical thesis by cand. Ing. Stephan Lederer at the Technische Universität Darmstadt within his studies of materials science. Stephan Weinbruch at the Institut für Angewandte Geowissenschaften, same faculty, is thanked for free access to the ESEM and Konrad Kandler for generously providing the ‘groupp’ classification software. The authors also like to thank Lothar Schütz at the University of Mainz and the German science foundation (DFG) for computational support. Particle images shown in this study were recorded at the Center for Electron Nanoscopy, Technical University of Denmark.

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INTRODUCTION

This work is based on data measured in Northern Finland, on the gateway to Arctic areas. It has been estimated that one aerosol component, black carbon, is responsible for 50 percent of the total temperature increases in the Arctic from 1890 to 2007 (Shindell and Faluveg, 2009). Aerosols affect climate directly by scattering solar radiation back to space and altering cloud optical and life time properties. In Arctic areas deposition of absorbing aerosol to snow and ice surfaces have also been estimated to have significant effect to climate (Quinn et al. 2008). The way that aerosol affects to Arctic climate depends not only on their properties, but also the time of the year they reach Arctic areas. This work concentrates on studying aerosol optical properties. These parameters are scattering and absorption coefficients, single scattering albedo and aerosol optical depth.

METHODS

Measurements were conducted in Pallas-Sodankylä Global Atmospheric Watch station in Northern Finland. The scattering coefficient is measured at three wavelength by nephelometer (model 3563, TSI, Inc., St. Paul, Minnesota), absorption coefficient at seven wavelength by Aethalometer (model AE31, Magee Scientific) and aerosol optical depth (AOD) in four wavelength with Precision Filter Radiometer (PFR, PMOD/WRC). Aethalometer and nephelometer are located at Pallas (67°58’N, 24°07’E, 565 m asl) and PFR in Sodankylä (67.37°N, 26.63°E, 179 m asl). The distance between the stations is about 120 km.

Data that is affected by malfunction of the instrumentation and peaks from very local sources like snowmobile exhausts are removed. Because the station at Pallas is occasionally inside a cloud, data with hourly average visibility below 5 km was removed. Nonidealities due to nonlambertian and truncation errors in nephelometer were corrected using the method described by Anderson and Ogren (1998). The aethalometer absorption measurement is known to suffer from a filter loading artefact. These artefacts can be corrected using different methods. Here, the approach presented by Weingartner et al. (2003) was chosen.

RESULTS

In figure (1) monthly averages over measurement period of scattering and absorption coefficient at wavelength of 550 nm are presented. Scattering and absorption coefficient have slight declining trend. Years 2008 and 2009 have clearly lower values than the overall average value of 13 1/Mm. Similar trend is also seen in absorption coefficient, but the time series is much shorter.

In figure (2) seasonal variation of absorption and scattering coefficient (left side), AOD and single scattering albedo (right side) are presented as monthly means. Scattering has maximum on August, which might be related to natural aerosol loading. Aerosol absorption coefficient has maximum on February and March, this is related to air masses from continental regions. Total extinction is dominated by scattering coefficients which are 6 and 20 times higher in winter and summer, respectively, than absorption coefficient. AOD has maximum values on March-May, this might be related to high AOD occasions with aerosol layers or thin clouds at higher troposphere since at Pallas ground based measurements show different behaviour, also in closer inspection of the data.
Scattering, absorption and AOD have their minimum on fall when aerosols are effectively washed out by more frequent rain than other seasons. SSA is clearly lower during winter than during summer which is most probably due to lower anthropogenic emissions of absorbing aerosols during summer time.

![Graph showing scattering and absorption coefficients over time](image1)

**Figure 1.** Scattering and absorption coefficients as a function of time.

![Graph showing annual variation of scattering and absorption coefficients at 550 nm and single scattering albedo (SSA) at 550 nm and AOD at 500 nm.](image2)

**Figure 2.** Annual variation of scattering and absorption coefficients at 550 nm (left side) and single scattering albedo (SSA) at 550 nm and AOD at 500 nm.

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DENSITY OF SATURATED, SUPERCOOLED AMORPHOUS WATER

J. MALILA¹ and J. HRUBY²

¹Department of Applied Physics, University of Eastern Finland, P.O. Box 1627, 70211 Kuopio, Finland
²Department of Thermodynamics, Institute of Thermomechanics AS CR, v.v.i., Dolejškova 5, 18200 Praha 8, Czech Republic

Keywords: density, water, supercooled, glassy.

INTRODUCTION

Whether clouds with temperature below 0 °C are composed of solid crystals, supercooled aqueous drops or glassy particles has a profound importance on the radiative transfer, heterophase chemistry and cloud–aerosol interactions in the tropo- and stratosphere (Baker, 1997; Bogdan et al., 2010). Micron-sized droplets of deeply supercooled water (down to 200 K) are observed in homogeneous nucleation studies (e.g. Wölk and Strey, 2001). Although droplets of substantially supercooled pure water are not observed outside the laboratory environment, strongly supercooled aqueous solutions are commonplace in the atmosphere, and properties of pure, supercooled amorphous (i.e. liquid or disordered solid) water are needed to provide the reference state for the evaluation of thermodynamic properties for such systems (Clegg and Wexler, 2011). Alas, it has turned out experimentally impossible to work with pure water samples at ambient pressure in the so-called no-man’s land between 150 and 235 K, as the crystallization into ice Ih or Ic takes place instantaneously when the sample is warmed or cooled into this region, and can be bypassed only when extremely high cooling rates are applied. Ways to overcome this problem include numerical simulations and experimental studies with aqueous solutions or water confined into nanoscopic structures, preventing critical nucleus of solid phase to emerge (for particularly concise introductions to the topic, see Cabane and Vuilleumier, 2005, and Ludwig, 2006). However, none of the proposed methods provides a perfect solution, and thus comparison of various methods is needed to reproduce the density of amorphous water at all temperatures relevant for clouds in polar tropo-, strato- and also mesospheres.

METHODS AND RESULTS

Topic of this abstract does not exactly present the most novel branch of science, as the first comprehensive review of available measurements of the density of liquid water below 0 °C was given by Mendeleev (1892). Below 136 K, amorphous water exists in three different glassy forms, distinguished by density: the variant with lowest density forms a metastable continuum with ordinary liquid water (Ludwig, 2006). The most well known of many anomalies of liquid water is its density maximum approximately at 277 K. As ordinary liquids become more dense when cooled, already Bridgman (1912) reasoned on thermodynamic grounds that density of supercooled water must also reach a minimum at some lower temperature, below which normal liquid behaviour is recovered.

We have reviewed available studies reporting density of amorphous water between ca. 20 and 300 K (Hrubý and Malila, 2011). These studies confirm Bridgman’s hypothesis, and show that the minimum in density is reached in the no-man’s land. We have fitted selected data—several data sets below the glass transition temperature 136 K and above the homogeneous nucleation temperature 235 K joined by a more speculative data set (Mallamace et al., 2007) combining diffraction measurements of glassy and bulk liquid water with samples confined into nanopores—with functional form based on a reference part for densities above 273 K, based on a modification of the one recommended the International Association of the Properties of Water...
Figure 1: A: Data used for the fit (different markers present different data sets, see Hrubý and Malila, 2011, for details) and the fitted correlation for the density $\rho$ as a function of temperature $T$; vertical lines from left to right divide ranges of glassy and highly viscous water, no-man’s land, and (supercooled) liquid water below density maximum. B: Comparison with some other proposed correlations, see text for details.

CONCLUSIONS

We have provided a new reference correlation for the density of water being in agreement with selected experimental data in range $20 < T/K < 273$, and being in reasonable agreement with the most accurate data sets also between $273$ K and $T_c$, thus being suitable for all applications in the atmospheric science. Furthermore, our study confirms the results of the more superficial analysis of Clegg and Wexler (2011), thus providing reliability into their correlations for aqueous solutions. However, further work is needed for glassy aqueous mixtures, not only of inorganic species relevant for stratospheric and upper tropospheric chemistry (Bogdan et al., 2010), but also on aqueous organic glasses being constituents of tropospheric aerosol particles at least in boreal and temperate climates (Virtanen et al., 2010). It is hoped that the proposed fit—together with those of other thermophysical properties of supercooled amorphous water (e.g. Murphy and Koop, 2005)—can also support these needs.
ACKNOWLEDGEMENTS

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WATER MASS TRANSFORMATION AND ICE PRODUCTION IN BILLEFJORDEN, SVALBARD

D. MOGENSEN\textsuperscript{1}, J. KINZEL\textsuperscript{2}, A. BOCK\textsuperscript{3}, S.M. KOLSTO\textsuperscript{4}, T.O. ROTHE\textsuperscript{4}, F. NILSEN\textsuperscript{5} and R. SKOGSETH\textsuperscript{5}

\textsuperscript{1} Division of Atmospheric Sciences, Department of Physics, P.O. Box 48, University of Helsinki, 00014, Finland.
\textsuperscript{2} University of Kiel, Germany.
\textsuperscript{3} University of Marburg, Germany.
\textsuperscript{4} University of Bergen, Norway.
\textsuperscript{5} The University Centre in Svalbard (UNIS), P.O. Box 156, N-9171 Longyearbyen, Norway.

Keywords: ICE PRODUCTION, POLYNYA MODEL, FJORD CIRCULATION PATTERNS, WINTER WATER FORMATION.

INTRODUCTION

As the global air and ocean temperatures increase, Arctic as well as Antarctic ice cover decrease. The change in ice cover extent is by far most significant and observable in summer. As late as in the summer 2011, Arctic sea ice extent reached the second lowest level ever measured (by satellite measurements since 1979) (National snow and ice data center: http://nsidc.org/index.html). Since Arctic ice cover measurements were started, the ice cover has always proven to be able to recover after summer time melting. However, during the past 10 years this has not been the case. \( \sim 42 \% \) decrease in multi year ice cover and a thinning of \( \sim 0.6 \) m in multi year ice thickness in the period 2005-2008 have been observed (Kwok et al., 2009).

A polynya is an area of open water surrounded by sea ice that stays unfrozen for most of the year. In these open areas frazil ice is produced. The ice is then transported away, leaving the polynya open to produce more ice. In case of very cold winters with slow wind, the polynyas will be covered by fast ice, decreasing ice production. Isfjorden, which is the site of our study, is an Arctic coastal polynya.

This study was carried out in Billefjorden, which is located in the North-East innermost part of Isfjorden, West Spitsbergen, Svalbard, Norway. Billefjorden is approximately 30 km long and 5 - 8 km wide. Since Isfjorden does not have any distinctive shallow sills at its mouth, it is directly linked to the shelf area along West Spitsbergen, where Atlantic water masses are guided from the West Spitsbergen Current towards the mouth of Isfjorden (Nilson et al., 2008). With a shallow sill at the mouth of Billefjorden, the fjord can keep locally produced brine water originated from the previous winters ice production. Billefjorden therefore works as an archive for last winters conditions in Isfjorden. Since the West Spitsbergen Current represents a major oceanic heat and salt input to the Arctic Ocean, we estimated the sea ice production in Isfjorden winter 2010 – 2011 based on the water masses in Billefjorden. Water masses were characterised and circulation patterns were identified.
METHODS

Measurements were conducted from 1 – 3 of July, 2011 in 12 different stations in Billefjorden, West Spitsbergen, Svalbard, Norway. CTD (conductivity, temperature and depth; type: Seabird Electronics SBE 19) measurements and bottom water samples (using a 2 l Niskin bottle) were obtained on board Viking Explorer. Further, a Seaguard Current Meter (ADCP; type: Aanderaa instruments) was installed on a fixed location in Billefjorden on board M/S Stalbas in order to measure physical water parameters as well as horizontal current velocities.

Further, an atmospherically forced 1D polynya model (Haarpaintner et al., 2001) was used for calculation of Isfjorden’s polynya activity.

RESULTS AND DISCUSSION

Water masses and water mass transformation

Depth profiles and TS – diagrams (temperature and salinity) for the 12 stations were investigated in order to classify the different water masses both along and cross Billefjorden. We identified Winter Cooled Water ($T < 0.5^\circ C$, $S > 34.4$) in the bottom water layers in Billefjorden. The water layer above mainly consists of Intermediate Water ($T > 1^\circ C$, $34.7 > S > 34$). A mixture of Intermediate Water and Transformed Atlantic Water ($T > 1^\circ C$, $S > 34.7$) is found in Isfjorden. The top layer typically consists of surface water ($T > 1^\circ C$, $S < 34$) with a deeper layer in Billefjorden towards the glacier, where the freshwater run-offs refresh the surface waters.

Isfjorden’s polynya activity: ice production in West Svalbard

Isfjorden’s polynya activity has previously been calculated based on measurements for every winter since 2000 (Nilsen et al., 2008). Using the same 1D polynya model, we have also calculated the activity for winter 2010-2011 and compared to previous activity values. The average polynya fraction was modelled to make up 99% of the total area, while the average spacial fraction of open water (frazil ice area) was modelled to make up 43%, thin ice 56% and fast/pack ice 1%. The largest contribution to accumulated sea ice production in the winter 2010-2011 is by frazil ice ($7.5 \times 10^9 m^3$), whereas thin ice (9%) and especially fast/pack ice (1%) only make up a minor fraction of the total accumulated sea ice volume ($8.2 \times 10^9 m^3$). Last winters high polynya activity in Isfjorden is also reflected in the large total accumulated salt released ($210 \times 10^9 m^3$), which is similar to the previous three winters.

Wind also has a large effect on polynya activity due to transport of frazil ice, whereby the polynya area is kept open. Wind speeds and -directions for winter 2010-2011 were analysed (data from LYR – Longyearbyen airport meteorological station was used). Out-fjord cumulative zonal wind speeds were found to be similar to those in 2005 (Nilsen et al., 2008), and are therefore the largest since 2000, favouring an out-fjord transport of newly formed sea ice.

High polynya activity favours surface cooling and thus convective overturning, resulting in dense bottom water masses in the Billefjorden basin. In Figure 1, we compare bottom temperature, salinity and resulting density for the winter season 2010-11 to the long term trend. Only the winters of 2007 and 2008 exhibit similar dense bottom water masses as in winter 2010-11. In contrast, bottom waters in winter 2009-2010 were freshest on a 5-year basis, reflecting strong interannual variability. This again emphasizes the efficiency of dense water mass formation in Billefjorden during the most recent winters, driven by a strong polynya activity.
CONCLUSIONS

Winter water formation during last winter in Isfjorden was effective compared to recent years. Model results show strong polynya activity for winter 2010-2011, creating large sea ice production and following large salt release. Further studies are needed in order to assess whether the strong polynya activity in winter 2011 has introduced a phase of large sea ice production and thus densification of bottom water masses in Billefjorden, possibly governing water mass properties during the upcoming years.

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CCN-PROPERTIES OF HULIS

R. MORTENSEN¹, T. B. KRISTENSEN¹, B. NEKAT², D. VAN PINXTEREN², A. G. HALLAR³ and M. BILDE¹

¹Dept. of Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark
²Leibniz-Institute for Tropospheric Research, Leipzig, 04318, Germany
³Desert Research Institute, Storm Peak Laboratory, Steamboat Springs, CO 80488, USA

Keywords: HULIS, CCN-activity, aerosol-cloud interactions.

INTRODUCTION

Humic-like Substances (HULIS) have been identified as a major fraction of the organic component of atmospheric aerosols. HULIS may affect aerosol properties due to their ability to nucleate cloud droplets (Dinar et al., 2006). HULIS are believed to form from biogenic and anthropogenic precursors and can be found in many environments e.g. marine (Krivacsy et al., 2001), urban (Salma et al., 2010), rural (Fors et al., 2010), remote environments (Feczek et al., 2007) and in firm from Antarctica (Cini et al., 1995). The knowledge about these substances in Arctic regions is very limited. The name HULIS originates from the fact that they are similar in structure to humic substances (HS) in soil and aquatic environments (Havers et al. 1998; Kiss et al. 2005). HS are complex mixtures of organic molecules with different sizes and similar structures. HULIS resemble HS in structure, content of carboxyl groups and aromatic moieties. However, it has been suggested that atmospheric HULIS consist of smaller compounds in terms of molecular weight with less aromatic moieties, higher surface activity and higher CCN-activity (e.g. Graber and Rudich, 2006; Salma et al., 2008). This study shows in agreement with Ziese et al. (2008) and Fors et al. (2010) that HULIS have similar CCN-activity as some HS reference fulvic acids like Suwannee River Fulvic Acid (SRFA).

To investigate the properties of HULIS, they have to be separated from the other components of atmospheric aerosol particles. Different extraction methods have been used in former studies resulting in different compositions of HULIS. The extraction method used in this study was introduced by Varga et al. (2001) and has been applied in several other studies (e.g. Wex et al., 2007; Ziese et al., 2008; Fors et al., 2010) even the final HULIS extract is known to contain some other polar organic compounds such as long-chain monocarboxylic acids, aromatic alcohols, or aldehydes (Limbeck, 2005).

In this study the CCN-activity of HULIS were investigated originating from different environments. The aerosols were obtained at a rural continental background site in Melpitz and at a mountain site located in Colorado called Storm Peak Laboratory (SPL). In addition, the investigation of HULIS from firm originating from the Greenlandic ice cap is an on-going study.

METHODS

Sampling: Melpitz:

24 hours samples are obtained at a continental background station located near the village Melpitz (51°32’N, 12°54’E). The filter samples were taken using a high volume sampler with a PM2.5 inlet at a flow rate of 0.5 m³/min⁻¹. Quartz fiber filters (MK 360, Munktell, Sweden, 15 cm diameter) were sampled from August 1 – 31, 2004.
SPL:
Free tropospheric aerosol samples were obtained at the Storm Peak Laboratory station located in Colorado 3220 m AMSL (40°27'N, 106°44'W) with a high volume sampler with a PM$_{2.5}$ inlet. The Teflon-impregnated glass fiber filters (T60A20, Pall Corporation, 8” x 10”) were sampled with a flow rate of 1 m$^3$/min. The measurement period was from July 30 to the August 1, 2010.

HULIS extraction:
The water soluble aerosol components were extracted by placing the filter pieces in Milli-Q water in an ultrasonic bath for 30 min. The water extracts were filtered through a syringe filter with a 0.45 µm pore size polyethersulfone membrane to remove filter fragments and suspended insoluble particles. The pH value of the extract was then adjusted to approx. 2.0 by addition of concentrated HCl, and loaded onto activated HLB solid phase extraction (SPE) columns (Oasis HLB 3 cc, Waters USA). Approx. 15 mL of filtrated extract was added to each column followed by 0.8 mL Milli-Q water (flow rate ≤ 1 mL min$^{-1}$) to rinse out any inorganic particulate matter and other polar organic compounds not retainable on the column. The retained organic compounds (HULIS and weak polar substances with lower molecular weight) were eluted with 5 - 7 mL methanol (≥ 99.9%) per column. The solvent of HULIS eluate was removed by a rotary evaporator. The dry HULIS were redissolved in Milli-Q water and stored at -18 °C until further analysis. The HULIS from Melpitz and SPL samples are referred to as Melpitz-HULIS and SPL-HULIS, respectively.

To check the purity of the extracted HULIS the concentration of inorganic ions and the total organic carbon were measured.

Experimental set-up:
The aerosols are produced by atomization of aqueous solutions, and then dried by using a diffusion drier and by dilution with filtered air. The aerosol flow is neutralized and reaches an electrostatic classifier (TSI, Model 3080) where it is size selected by the DMA. Last the quasi-monodisperse aerosol flow is divided between a condensation particle counter (CPC) (TSI, Model 3010) and a cloud condensation nucleus counter (CCNC) (DMT, Model CCN - 100). The number concentration of activated particles (measured by the CCNC) divided by the total particle number concentration (measured by the CPC) is called the activated fraction. The CCN-activity is then derived from a sigmoidal fitting curve of the activated fraction of particles plotted against the particle diameter, where doubly charged particles are accounted for. The supersaturation that is necessary to activate a particle with a given size and composition, is the critical supersaturation (SSc).

RESULTS

In Figure 1 are shown some of the CCN-activities of HULIS and the reference compound SRFA from the literature. There can be seen a wide distribution of results, e.g. at a SSc of approx. 0.2%, Dinar et al. (2006) find the HULIS particles to activate at approx. 80 nm, while Ziese et al. (2008) find them to activate at approx. 160 nm. Probably the main reason for the deviations in CCN-activity is Dinar et al. (2006) used a different extraction method than the other studies. Different environments, different sources of HULIS and ageing can have an effect on the CCN-activity as well, e.g. HULIS samples from fresh smoke aerosols (blue triangles) have a lower CCN-activity compared to slightly aged smoke aerosols (blue plus signs), hence ageing increases activity (Dinar et al., 2006). A contamination caused by inorganics is another possible reason for the differences. Unfortunately, the studies do not report the content of inorganic ions to support this argument.

Figure 1 also shows that the more recent studies on HULIS have a CCN-activity similar to the reference compound SRFA.
CONCLUSIONS

The CCN-activity of atmospheric HULIS samples have been investigated and compared with literature data. Our results show that HULIS extracted by the Varga method (Varga et al. 2001) are significantly less CCN-active than ammonium sulphate for the two different samples of Melpitz and SPL. Future work will include investigation of HULIS samples obtained in arctic regions.

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investigation of their effects on surface tension with two models linking H-TDMA to CCNC data.


IN SITU MEASUREMENTS OF SEA SPRAY AEROSOL EMISSIONS WITH THE EDDY COVARIANCE METHOD AT SVALBARD (78.9°N)

E. M. MÅRTENSSON¹,² AND E. D. NILSSON¹

¹Department of Applied Environmental Research, Stockholm University, Sweden
²Department of Earth Sciences, Uppsala University, S-752 36 Uppsala, Sweden

Keywords: Primary marine aerosols, sea spray, eddy covariance, air-sea exchange, Arctic Ocean

INTRODUCTION

The major source of the primary marine aerosol is breaking waves. The aerosol particles are emitted from the water surface into the atmosphere directly as droplets with the composition of seawater enriched with marine organic compounds, bacteria and viruses. With climate change affecting temperature, wind, and ice, the key physical factors driving the sea spray emissions, the production of primary marine aerosols is expected to change. In situ emission data from Arctic waters are required in order to validate or improve the existing sea spray parameterization for cold waters, Mårtensson et al. (2003). Such improvements or validations are important in order to estimate the over-all sea spray source in a changing climate (Struthers et al., current issue) and represent this large aerosol source in climate models (e.g. Struthers et al., 2011). During the Greenhouse Arctic Ocean and Climate Effect of Aerosols (GRACE) first field campaign in the summer 2009 direct flux measurements were made from a 10 meter mast on the peninsula Brøggerhalvøya at Svalbard (78.938N, 11.3406E). The campaigns also included in situ tank experiment of sea spray production (Zabori et al., current issue). The project objective is to assess the effects of decreasing sea ice upon aerosol and cloud climate forcing over a future Arctic Ocean in an increasingly warmer climate. Sea spray production can be expected to change in response to reduced sea ice, increasing temperature and changes in wind speed.

Figure 1. Overview map of Svalbard (left side) and detailed map of Kongsfjorden with surroundings (right side). (1) marks the flux mast at Brøggerhalvøya, (2) the Kings bay marine laboratory.
METHOD

The most direct method to quantify the aerosol emissions is the eddy covariance flux method. It has previously been used to study sea spray emissions (Nilsson et al., 2001; Geever et al., 2005), urban traffic emissions (Mårtensson et al., 2005; Vogt et al., 2011a,b,c), and emissions from the Amazonas (Ahlm et al., 2010). Similar measurements were made during the GRACE field campaign in the summer 2009. Fluctuations in the vertical wind ($w'$) and aerosol/gas concentration ($c'$) were sampled and processed so that the covariance $<c'w'>$ equals the aerosol/gas fluxes. The measurements were made on the peninsula Brøggerhalvøya at Svalbard (78.938 N, 11.3406 E). The mast was 10 meter high; a Gill HS-50 ultrasonic anemometer measured the vertical and horizontal wind speed. The size resolved aerosol particle concentrations were measured from 0.25 to 2.5µm diameter with two GRIMM 1.109 Optical Particle Counters (OPC).

RESULTS

From the ocean wind sector the upward fluxes totally dominated the aerosol fluxes in the OPC range, to a higher degree than any previous data set we have worked on. This is probably due to the low back ground aerosol concentrations, which minimise the aerosol deposition fluxes. The results show a clear wind dependence. In Figure 2 the number flux in the OPC range are shown as a function of wind speed averaged over 1 ms$^{-1}$ wind speed bins.

![Figure 2. Particle median emission as function of wind speed. The vertical bars shows 25 and 75 percentiles. Dashed curves show the source parameterisation according to Mårtensson et al. (2003) for 3°C (blue) and 5°C (red) sea surface temperature.](image)

Figure 2 agree fairly well with previously studies as it show a nearly exponential wind dependency of the sea spray flux (compare with Nilsson et al. (2001) and Geezer et al. (2005)), which is nearly linear on a log-linear scale. The new results are not significantly different to the sea salt source parameterization by
Martens son et al. (2003), considering the sea temperature during the GRACE campaign, and the variation in the data.

Figure 3 show the average size distribution of the observed aerosol fluxes. It agree qualitatively with previous studies in the sense that the emission flux increase with decreasing diameter in the 0.1 to 1 µm diameter range (Martens son et al., 2003; Haultin et al., 2010,2011; Zadora, this issue). Further work is however needed in order to determine how good or bad the agreement is quantitatively.

![Figure 3. Average aerosol number flux size distributions from the coastal sector. The vertical bars shows 25 and 75 percentiles.](image-url)

**CONCLUSIONS**

These in situ sea spray fluxes are the most northern over open Arctic waters since Nilsson et al. (2001), and the first providing size resolved fluxes over open sea at these latitudes. They confirm that the wind is the dominant driving force behind sea spray emissions (which would only come second to sea ice cover, which effectively reduce the emissions). It is currently not clear if we can distinguish any difference due to season or water temperature, but at least we can say that such effects are weaker than the influence of wind speed. Further work on this data set includes the interpretation of the parallel flux measurements at different air temperature (heated up to 400°C), which may reveal indirectly information of the chemical composition of the particles, and comparison with existing sea spray source parameterisation.

**ACKNOWLEDGEMENTS**

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PHOTOPROTECTIVE ROLE OF EPICUTICULAR WAXES IN BOREAL SCOTS PINE (PINUS SYLVESTRIS L.)

B. OLASCOAGA, J.A. PORCAR-CASTELL, E. JUUROLA, J. BÄCK and E. NIKINMAA

Department of Forest Sciences, University of Helsinki, P.O. BOX 27, 00014 Helsinki, Finland.

Keywords: epicuticular waxes, PAR, Scots pine (Pinus sylvestris L.), spectroradiometer.

INTRODUCTION

Cuticular waxes are a complex mixture of long-chain aliphatic compounds that include alkanes, aldehydes, esters, ketones, primary alcohols, secondary alcohols and other derived compounds, that work as a barrier between the plant tissues and environment. The fraction of waxes embedded in the cuticle is classified as intracuticular waxes, whereas those on the surface are designated as epicuticular waxes and often tend to aggregate generating crystalline structures of diverse shape that emerge from the cuticle surface.

Both types of waxes vary in molecular fraction and composition (Jetter et al., 2000; Shepherd and Griffiths, 2006) and thought to play different roles: intracuticular waxes mainly function as water transpiration barrier (Schönherr, 1976; Riederer and Schreiber, 1995) whereas epicuticular waxes exhibit allelopathic properties as been reported to influence fungal development on leave surface (Flaishman et al., 1995) and alter insect behavior (Städler, 1986). Epicuticular waxes also strongly influence on leaf wettability, self-cleaning behavior and light reflection (Koch and Enskiat, 2008). Although visible light reflection by epicuticular waxes has been analyzed in some crop and tree species, it has been only characterized within a period of few weeks from fully developed leaves (Baker, 1974; Reicosky and Hanover, 1978). Longer studies on changes in visible light reflection by epicuticular waxes in natural conditions might reveal a more realistic view about the role of epicuticular waxes that might be linked to plant photosynthesis and photoprotection.

In this study we analyzed annual differences on visible light absorption by epicuticular waxes for different needle ages and canopy positions in boreal Scots pine (Pinus sylvestris L.) trees.

METHODS

Needle samples were collected from SMEAR II Station (61° 31’ N, 24° 17’ E, 180 m a.s.l) in the vicinity of Hyytiälä Forestry Field Station in Southern Finland during the period August 2010 to June 2011.

Eight 48 year-old and c. 15 m tall Scots pine trees were studied and accessed through permanent scaffold towers. In each tree, two canopy levels were chosen for sampling: top-canopy, corresponding to the three first living whorls (c. 15m), and low-canopy, from the last three living whorls (c.7m). Sampling was carried out for current year, one-, and two-year-old needles from the same branches.

The samplings were carried out four times, corresponding each to the end of each season. Thus: summer, 19-20th August 2010; autumn, 22-24th November 2010; winter, 21-23rd February 2011, and spring, 09-11th June 2011.

Reflectance spectra data from each needle sample were recorded using a portable spectroradiometer (ASD FieldSpec® HH VIS-NIR) combined with a plant probe with halogen light source and a fiber optic cable.

Needles were attached and distributed evenly in a black Hansatech leaf-clip® that perfectly fitted with
the plant probe. Reflectance spectra from the same sample were recorded before and after wax was removed by dipping the needles in a chloroform bath for 10 s (Fig.1).

Absorption spectra from each needle sample were derived from the original reflectance spectra assuming near zero transmittance for visible light in Scots pine needles. Average visible light absorption value was estimated by integrating the data between 400 and 700 nm.

**DISCUSSION**

Reflectance spectra from PAR region (Fig.1) were transformed into PAR absorption spectra assuming near zero transmittance as reported by Cameron (1970) for some tree species. Light reflection profiles were similar in shape to those obtained for other species of deciduous and perennial trees, and crop species (Rabideau *et al.*, 1964).

![Figure 1](image1.png)

*Figure 1.* Reflectance spectra from visible light (PAR) (400-700 nm) to near infrared (NIR) light (>700 nm) before (dark grey) and after (light grey) wax removal by 10 s chloroform bath. Profiles show current year and top-canopy Scots pine needles from summer 2010.

![Figure 2](image2.png)

*Figure 2.* PAR absorption from epicuticular waxes for: a) top-canopy (c.15 m), and b) low-canopy Scots pine needles. Abbrev.: 0) current year needles, 1) one-year-old needle, 2) two-year-old needles (s) summer, (w) winter, (a) autumn, (sp) spring. Each value represents the mean ± standard error (n=8). Each tree’s value is the average of 4 repetitions. The three needle ages were sampled during year 2010-2011 but are represented as a continuum in the graph.

Average absorption values from 400 to 700 nm showed that the highest peak in PAR absorption for epicuticular waxes was obtained in top-canopy current needles during summer (Fig. 2a), after spring bud break and needle expansion of elongation was completed, and decreased till winter. The same pattern was registered for both current- and 1-year-old needles. Seasonal and annual reductions in
PAR absorption might be consequence of changes in the amount of waxes, differences in the molecular composition or/and alteration in epicuticular wax crystal conformation.

In conifers, the amount of wax changes with leaf age (Cape et al., 1989; Percy et al., 1993) together with the morphology and chemical composition (Crossley and Fowler, 1986; Percy et al., 1993; Günthardt-Goerg 1994; Jetter and Schäffer, 2001). Nevertheless, only a few studies comparing the effect on epicuticular waxes for periods longer than a few months from needle expansion have been carried out in the field. Thus, further investigation is needed to fully understand the importance of the phenomena throughout time.

Needle position in the crown seems to have effects on light absorption as similar absorption patterns but lower values were obtained for low-canopy needles (Fig. 2b). In many species, the amount of wax increases with branch height (Sase et al., 1998; Cameron et al., 2006) and insolation would be a possible factor that influences the amount of epicuticular wax (Cape and Percy, 1993). Increased wax thickness has been reported for developing leaves in crops and tree species after an increment in light irradiation (Baker, 1974; Reed and Tukey, 1982; Shepherd et al., 1995; Reed and Tukey, 1982; Giese, 1975). Nevertheless, most of the studies have been focusing on linking epicuticular waxes to effects of climatic stress (i.e. drought, UV radiation increase) or air pollutant stress (i.e. acid mist, urban pollution), been carried out in seedlings and saplings, and often, under controlled conditions (Turunen and Huttunen, 1990; Cape and Percy, 1993). There are no studies analyzing the influence of PAR light on epicuticular waxes.

In this study an increase in PAR absorption was detected in current- and 1-year-old needles for both canopy positions from winter to spring (Fig. 2). This pattern might reflect a photoprotective role of epicuticular waxes in minimizing the excitation energy and damage to photochemical machinery and photochemical reaction centers, when bright days and the albedo effect from the snow increase light irradiance to needles that still have suppressed their overwintered photosynthetic machinery.

In most species, wax production appears to occur during leaves first growing season, and conifers are thought to follow the same pattern (Cape and Percy, 1993; Güntherd-Göerg, 1987; Percy and Baker, 1990; Percy, Jensen and McQuattie, 1992). Nevertheless, Sase et al., (1998) registered a slight wax load increase during the second growing season in current needles of the conifer Cryptomeria japonica.

Further investigation about annual amount, composition and structure of epicuticular waxes in natural conditions is necessary to fully understand the role that surface waxes play in photoprotection and regulating plant light requirements.

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INTRODUCTION

Atmospheric aerosol particles have both climatic (IPCC, 2007) and health related effects (von Klot et al. 2005). A multitude of sources produce the suspended aerosol particle population, which varies both temporally, spatially and as a function of height (O’Dowd et al. 2007, Hermann et al. 2008, O’Dowd et al. 2009). One of the sources is forest fires, which affect via long-range transport the air quality in the Arctic areas (Paris et al., 2010, Saarnio et al., 2010).

The measurements presented in this study were performed in July 2010 during two remarkable episodes with air mass trajectories from East-Southeast to Finland. The aim was to determine the aerosol particle total number concentrations, $CO_2$ - and $H_2O$-gas concentrations and meteorological parameters from ground level up to 3500 meters in Finland during forest fire episodes.

METHODS

The results that are presented here are based on the data collected by an airborne measurement platform. The aircraft used is a light airplane, Cessna FR172F. The instruments had been built into a rack behind the front row seats in the plane. The sample air was piped into plane via an inlet that was located plane’s right wing. The inlet was designed according to… Aerosol instrumentation included an ultrafine particle counter (model 3776 CPC, TSI Inc.) with a cut-off at 3 nm (Mordas et al. 2008). This instrument provided us the total number concentration of the sub-micron particles. The meteorological parameters, like temperature, relative humidity and pressure as well as concentration of water vapor and carbon dioxide with a Li-Cor Li-840 were also measured.
Airborne measurements were performed previously with partly similar installation described in Schobesberger et al., 2009.

PRELIMINARY RESULTS AND DISCUSSION

Figure 1. Four vertical flight profiles of aerosol total number concentration and $CO_2$ operated to South Finland during extensive wildfires in Russia in late July. The arrows represent the smoke layer detected over the Jämsä area.
During summer 2010, there were several hundred of forest fires in Russia due to high temperatures and drought. Primarily forest fires raged in the west Russia, near to Moscow, starting in late July 2010.

Our measurement route with the Cessna aircraft went from Savonlinna to Tampere through Jämsä or Eastern and Southern Finland during the first days of intense forest fires. Figure 1 presents a selection of two descents and ascents during the flights. During the flights, the weather was sunny and warm but hazy even at altitudes up to 3.8 km. There were clouds high, not at all down. Air masses came to Finland from Southeast at altitudes 3 km and from Southeast or East at altitudes 500 meters, respectively. In the first climb and descent, we did not observe any different results compared typical smokeless air, but during the latter profiles particle concentrations went up to $10^4 \, \text{cm}^{-3}$ at altitudes 2.5 – 3.8 km supported HYSPLIT backtrajectories indicating an airmass from the Russian forest fire area. The carbon dioxide concentrations did not diverge strikingly from a normal during Russian forest fires but there were some layers of increased mixing ratios especially at altitudes under 2 km.

In the future we aim to connect our airborne measurements with specific source areas via satellite forest fire imagery as well as compare the forest fire flight data to profiles obtained in the clean air masses.

**CONCLUSIONS**

The measurements of emissions from several forest fires in Russia during summer 2010 were performed by small single engine aircraft, Cessna. The flights were operated to Eastern Finland. Results showed the high particle concentrations at the altitudes 2.5 – 3.8 km which were supporting the forecasts. During two measuring days, we performed 16 vertical profiles all together, from 300 meters up to 3.8 kilometers. During the analyzed profiles (Figure 1), air masses came to Finland from East or Southeast, namely the presence of Russian wildfires.

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THE ANALYSIS OF SIZE-SEGREGATED CLOUD CONDENSATION NUCLEI COUNTER (CCNC) DATA FROM SMEAR II AND ITS IMPLICATIONS FOR AEROSOL-CLOUD RELATIONS

M. PARAMONOV\textsuperscript{1}, T. PETÄJÄ\textsuperscript{1}, P.P. AALTO\textsuperscript{1}, M. DAL MASO\textsuperscript{1}, N. PRISLE\textsuperscript{1}, V.-M. KERMINEN\textsuperscript{2} and M. KULMALA\textsuperscript{1}

\textsuperscript{1}Department of Physics, University of Helsinki, P.O. Box 64, FI-00014, Helsinki, Finland.
\textsuperscript{2}Finnish Meteorological Institute, P.O. Box 503, 00101, Helsinki, Finland.

Keywords: CCNC, aerosol, cloud, critical diameter, hygroscopicity.

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

CCNC measurements have been conducted continuously at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) in Hyytiälä Forestry Field Station in Finland since June 2008, and they form a part of the comprehensive network of aerosol- and meteorology-related measurements in Southern Finland (Hari and Kulmala, 2005). The station (61º 50' 50.685''N, 24º 17' 41.206''E, 179 m a.m.s.l.) is located 220 km north-west of Helsinki on a flat terrain surrounded by a Scots Pine stand, and is, therefore, well representative of the boreal environment. 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. Both non-size-segregated and size-segregated measurements are performed by the instrument, with the latter having started in February 2009 with an introduction of a DMA into the system. CCN concentrations are measured across 30 size channels, with particle diameters ranging from 20 to 300 nm for supersaturation levels of 0.1%, 0.2%, 0.4%, 0.6% and 1%. From July 2010 until May 2011 the instrument was operating at levels of SS different to those of factory calibration mentioned above, namely 0.0859%, 0.216%, 0.478%, 0.74% and 1.26%. The measurement setup allows for a direct determination of critical diameter $D_c$ and the hygroscopicity parameter $\kappa$. The dataset consisted of data collected by CCNC from February 2009 up to July 2011.

Activated fractions $A$ were calculated for each size channel in each spectrum by dividing the number concentration of CCN by the corresponding number concentration of CN. Each CCN efficiency spectrum was then fitted with a function proposed by Rose et al. (2008) in the form of

$$ A = a \left( 1 + \text{erf} \left( \frac{D-D_a}{\sigma \sqrt{2}} \right) \right) \quad (1), $$

where $a$ is half the maximum $A$ for each spectrum, $\text{erf}$ is error function, $D$ is particle diameter, $D_a$ is the particle diameter at $A = a$ and $\sigma$ is the standard deviation of the cumulative Gaussian distribution function. In the function above the fit parameter $D_a$ is the critical diameter of dry aerosol particles $D_c$, which in this study is defined as the diameter at which half of the incoming particles are activated at a certain level of
supersaturation. The original fitting method was carried out as per Rose et al. (2008), in which $A$ values were normalized to unity by multiplying every $A$ in the CCN efficiency spectrum with $0.5/a$, and $D_a$ and $σ$ were the fit parameters in the function. Since ambient aerosol is often externally mixed, any given CCN efficiency spectrum does not necessarily level out at the activated fraction $A=1$; this, in some cases, led to an inappropriate fit of the function to the data and the overestimation of $D_c$ for all levels of SS. Following this discovery, a new method is suggested, in which the observed activated fractions $A$ are used (no normalization) and the value of $a$ in Eq. 1 is also a fit parameter together with $D_a$ and $σ$. Hereafter, the two methods are referred to as old and new methods.

Hygroscopicity parameter $κ$ was then calculated for each pair of critical diameters and levels of SS using the following equation from Rose et al. (2008):

$$s = \frac{D_{wet}^3 - D_3^3}{D_{wet}^3 - D_3^3(1 - κ)} \exp \left( \frac{4σ_{sol}M_w}{RTρ_wD_{wet}} \right)$$

(2)

where $s$ is the water vapour saturation ratio, $D_3$ is the dry particle diameter, substituted with $D_a$, $D_{wet}$ is the droplet diameter, $σ_{sol}$ is the surface tension of condensing solution (taken that of pure water), $M_w$ is the molar mass of water, $R$ is the universal gas constant, $T$ is the absolute temperature, and $ρ_w$ is the density of water. $κ$ values were determined by varying $κ$ and $D_{wet}$ so that $s$ is equal to the prescribed supersaturation and to the maximum of the Köhler model curve of CCN activation.

Critical diameters were calculated using both old and new methods, and hygroscopicity parameters $κ$ were calculated for both sets of critical diameters (both also referred to hereafter as old and new).

RESULTS

As mentioned previously, the old method of calculating $D_c$ produced consistently higher values than the new method; this was true for all SS levels (Table 1). Normalizing $A$ to unity forced the function to level out at $A=1$, which in reality may not always be the case. In many instances, due to the aerosol being externally mixed, even the larger particles did not all activate completely and the observed $A$ values reached a maximum of less than 1, e.g., 0.9 (Fig. 1).

Table 1. Critical diameter $D_c$ from two methods at different supersaturations.

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<th>Old $D_{50}$</th>
<th>New $D_{50}$</th>
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</tbody>
</table>

The old method was particularly inappropriate for higher SS levels due to a large scatter of $A$ values. The new method produced the best fitting to the data, as discovered by the analysis of root mean square error (RMSE). However, it did not fit correctly in some cases of lowest SS, where the observed $A$ reach their maximum at the largest sizes, and, therefore, no upper plateau existed. Since $a$ was fit parameter in the new method, the function did not, as such, have an upper limit. Therefore, in cases described above, the function produced very high $D_c$ values (although the RMSE was still better).
Figure 1. Sample CCN efficiency spectrum and two ways to determine $D_c$ (left panel - old method, right panel - new method).

These two main differences of old and new fitting methods are clearly seen in Figure 2. The analysis of monthly variation of critical diameters clearly showed the annual trend for $D_c$ at lowest SS (largest particles). With a clear minimum at the end of winter, critical diameters increase to reach their maximum in late summer. This annual trend indicates that a particle of the same diameter is more hygroscopic in the winter than in the summer. This will later be shown in the monthly variation of $\kappa$. No diurnal variation of $D_c$ was found.

Figure 2. Critical diameters $D_c$ from two methods.

An overall average $\kappa$ for aerosol particles at SMEAR II was determined to be 0.18 and 0.29 for old and new methods, respectively, clearly indicating the presence of organic species within the particles. The old method produced the exact same value as was reported by Sihto et al. (2010) for the same location; both
of these values fall within the range of 0.27±0.21 reported by Pringle et al. (2010) for continental aerosol. While the old method and the results by Sihto et al. (2010) indicate that aerosol particles in Hyytiälä are fairly non-hygroscopic, the new method, if proven to be a valuable method, points to a higher hygroscopicity of aerosol particles in boreal environment than previously thought. Figure 3 presents the monthly variation of \( \kappa \) from old and new methods for two levels of SS. As expected, hygroscopicity of particles is largest in February and smallest in July-August, corresponding well with the observed monthly variation of \( D_c \). The annual trend in \( D_c \) and \( \kappa \) is mostly pronounced for larger particles, indicating that over the course of the year the chemical composition of smaller particles remains the same, while larger particles exhibit changes in their chemical composition. Considering that typical levels of supersaturation inside the cloud are small (~0.1%) (Pruppacher and Klett, 1996) and, therefore, particles that activate as cloud droplets are the larger ones (>150 nm), the variation in their chemical composition throughout the year plays a crucial role in cloud formation and determination of their exact hygroscopicity becomes an important task. No diurnal variation of \( \kappa \) was found.

The subject in question is an ongoing project, aiming at increasing the understanding of physical and chemical properties of CCN-size aerosol in a boreal environment, as well as improving the methodology for deriving these physical and chemical properties. Several questions remain open. The new method produced smaller critical diameters (Fig. 2), yet average hygroscopicity parameter \( \kappa \) is higher (Fig. 3); this issue is currently under investigation. Several other upcoming questions include the source apportionment of particles of different hygroscopicity levels and a detailed chemical speciation of particles acting as CCN using various instrumentation.

ACKNOWLEDGEMENTS

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INTRODUCTION

Clouds are recognised as one of the most important modulators of radiative processes in the atmosphere (Platnick and Twomey, 1994). In order to assess the impact of aerosols on clouds in the climate system, it is crucial to understand the underlying physical processes governing cloud-aerosol interactions. The aerosol indirect effect, i.e. the change in cloud albedo due to a change in the atmospheric aerosol concentration remains one of the largest sources of uncertainty when estimating the anthropogenic influence on climate. For example, there is still no consensus on the relative importance of size and composition for the cloud droplet nucleating ability of aerosol particles (Dusek et al., 2006; McFiggans et al., 2006). The difficulty in untangling relationships among aerosols, clouds and precipitation has been partly attributed to the inadequacy of existing tools and methodologies (Stevens and Feingold, 2009).

Numerous cloud-aerosol modeling sensitivity studies have been conducted (e.g. Feingold, 2003), however, few have used detailed statistical methods to investigate the global sensitivity of a cloud model to input aerosol parameters (Anttila and Kerminen, 2007; Partridge et al., 2011a, b). Global sensitivity analysis considers parameter changes over the entire multi-dimensional parameter domain. This generally leads to different, but more reliable results because parameter sensitivities in non-linear models of complex systems typically vary considerably over the feasible space of solutions.

One approach to global sensitivity analysis of cloud-aerosol interactions is to embrace an inverse modeling approach and invoke posterior probability density functions of model parameters using Markov Chain Monte Carlo simulation (MCMC) (Partridge et al., 2011b). Such methods not only provide an estimate of the best parameter values, but also a sample set of the underlying (posterior) uncertainty.

METHODS

For the efficient investigation the cloud-aerosol inverse problem we couple a state of the art self adaptive DiffeRential Evolution Adaptive Metropolis algorithm (DREAM) (Vrugt et al., 2009) to an adiabatic cloud parcel model (Roelofs and Jongen, 2004). For a more detailed description of both the MCMC algorithm and the cloud parcel model, the reader is referred to P11b. To benchmark our MCMC framework, it is useful to start the inverse modeling analysis with numerically generated cloud data (i.e. “synthetic” calibration data) simulated using known values of the model parameters (calibration parameters). In this study we focus on investigating the sensitivity of the lognormal aerosol parameters...
describing the accumulation mode (number, size and shape) as well as the chemistry (soluble mass fraction). For each of the base simulations we keep the updraft velocity fixed to 0.3 ms\(^{-1}\). In order to investigate the influence of environmental conditions on the posterior distribution and sensitivity of the governing adiabatic cloud parcel model parameters we synthetically generate cloud droplet size distributions using input from four different aerosol environments (Table 1). The DREAM algorithm was then used to find those values of the pseudo-adiabatic cloud parcel parameters that provide the best possible fit to the measured droplet size distribution. This results in an ensemble of parameter values that define the posterior distribution from which we can obtain global sensitivity.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Marine Arctic</th>
<th>Marine Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration Parameter</td>
<td>Lower Limit</td>
<td>True Value</td>
</tr>
<tr>
<td>N2 (cm(^{-3}))</td>
<td>36.50</td>
<td>74.50</td>
</tr>
<tr>
<td>R2 (nm)</td>
<td>35.00</td>
<td>48.00</td>
</tr>
<tr>
<td>GSD2</td>
<td>1.50</td>
<td>1.68</td>
</tr>
<tr>
<td>Sol MF</td>
<td>0.30</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table 1. Aerosol physiochemical adiabatic cloud model parameter values used to generate synthetic cloud droplet size distribution measurements, as well as their respective lower and upper bounds used to create posterior distributions derived with DREAM. N2: accumulation mode number concentration; R2: accumulation mode mean radius; GSD2: accumulation mode geometric standard deviation; Sol MF: soluble mass fraction.

RESULTS

We calculate the relative sensitivity between the parameters by investigating the posterior distribution of the four calibration parameters for each of the four aerosol environments (Fig. 1). A larger normalised posterior range represents smaller sensitivity to a calibration parameter. For marine average aerosol conditions (Fig. 1b) the particle concentration of the accumulation mode is the most important parameter for the activation of cloud droplets. The geometric standard deviation of the accumulation mode and soluble mass fraction are least important. For marine Arctic conditions (Fig. 1a) the results are similar; however, the geometric standard deviation is of larger importance. The low sensitivity to chemistry in clean environments is intuitive; it does not matter how soluble a particle is if it does not exist. Thus, the number of particles must be, up to a certain threshold the limiting factor in any environment for the cloud droplet nucleating ability of an aerosol population. This is also consistent with current observations and theory for cleaner environments (e.g. Dusek et al., 2006).

For rural continental conditions, the overall picture is the same, the number of aerosol particles in the accumulation mode is still the key parameter and the soluble mass fraction is the least important calibration parameter (Fig. 1c). However, now the soluble mass fraction is relatively more important. The geometric standard deviation is of equal importance as the mean radius, and there is a dramatic increase in the accumulation mode number normalised posterior range compared to marine general conditions. Moving to a yet further polluted environment (Fig. 1d) we see a shift in the dominant parameter for describing droplet activation to the parameter representing particle chemistry, with the difference between sensitivity of the lognormal aerosol parameters describing the accumulation mode decreasing further.
Thus the results highlight that for the adiabatic cloud parcel model used in this study having a fixed updraft velocity of 0.3 m s⁻¹ there is a clear tipping point in the calibration parameter sensitivity between marine average and rural continental aerosol conditions.

![Figure 1](image1.png)

Figure 1. Normalized posterior parameter ranges for a) Marine Arctic aerosol environment, b) Marine Average aerosol environment, c) Rural Continental aerosol environment, and d) Polluted continental aerosol environment. The last 20% of the samples generated with DREAM were used to derive the results. The y-axes are scaled between 0 and 1 using the prior ranges defined in Table 1 to yield normalized ranges. The blue error-bars represent the 1%-99% limits of the posterior distribution. The blue circles are used to signify the maximum likelihood values of the parameters that provide the closest fit (lowest RMSE) to the measured aerosol size distribution, whereas the red circles denote the true parameter values used to create the synthetic data. Each grey line going from left to right through each panel is a different parameter sample from the posterior distribution.

Further simulations were performed to investigate the effect of the base updraft velocity on the parameter sensitivity (Fig. 2). From these results it is demonstrated that the relative sensitivity of the chemistry is a strong function of the prevailing meteorological conditions and number of accumulation mode particles. It is clear that the relative importance of the chemistry compared to the accumulation mode radius increases for all aerosol environments when the updraft is halved (Fig. 2a).
Figure 2. Parameter relative sensitivity for a) Updraft = 0.15 m s\(^{-1}\), b) Updraft = 0.30 m s\(^{-1}\), c) Updraft = 0.60 m s\(^{-1}\). The last 20% of the samples generated with DREAM were used to derive the results. The y-axes NPR labels correspond to “Normalized posterior parameter range”. Thus, we present the relative sensitivity for each parameter as the aerosol environment becomes more polluted. A higher value of 1-NPR indicates a parameter having higher relative sensitivity. Going from left the light the x-axes corresponds to the accumulation mode number of marine Arctic, marine average, rural continental, and polluted continental conditions respectively.

CONCLUSIONS

The employed analysis method provides a new, integrative framework to evaluate the sensitivity of the derived droplet size distribution to the input parameters describing the lognormal properties of the accumulation mode and the particle chemistry. This study demonstrates that inverse modelling provides a flexible, transparent and integrative method for efficiently exploring cloud-aerosol interactions efficiently with respect to parameter sensitivity and correlation.

The applied algorithm shows that for marine Arctic and marine general aerosol conditions the aerosol particle size and mean radius of the accumulation mode are the most important parameters when simulating the cloud droplet number concentrations, whereas the chemical composition is the least important. There is a clear transition in the inverse modeling results from very clean marine Arctic aerosol conditions to polluted continental For the present updraft applied (0.3 m s\(^{-1}\)) in more polluted environments (aerosol concentration of the accumulation mode > 400 cm\(^{-3}\)) the relative importance of the soluble mass fraction increases considerably. For the rural polluted aerosol environment (aerosol concentration of the accumulation mode > 1000 cm\(^{-3}\)) chemistry dominates the lognormal aerosol parameters describing the accumulation mode. Further simulations were performed to investigate the effect of the base updraft velocity on the parameter sensitivity which showed that the relative sensitivity of the chemistry is a strong function of the prevailing meteorological conditions and number of accumulation mode particles.

Whilst these main conclusions mostly confirm those obtained by previous studies, the method presented considers and displays a number of important findings in an integrative way, providing a visually clear way to deconstruct complex cloud-aerosol interactions into a visually simple form.
ACKNOWLEDGEMENTS

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WRF-Chem Simulations of Aerosol - Cloud - Water Vapor Interactions in Warm and Mixed-Phase Clouds

M.A. Pfeffer\textsuperscript{1}, J.E. Kristjansson\textsuperscript{1}, F. Stordal\textsuperscript{1}, T. Berntsen\textsuperscript{1}, C. Zhao\textsuperscript{2} and J. Fast\textsuperscript{2}

\textsuperscript{1} University of Oslo, Department of Geosciences, Oslo, Norway.
\textsuperscript{2} Pacific Northwest National Laboratory, Richland, WA, USA.

Keywords: WRF model, Aerosol-cloud interactions, Water Vapor, Radiation.

Warm Maritime Clouds

The WRF-Chem atmospheric model has been used to quantify aerosol-cloud-water vapor feedbacks. Simulations of warm, typical trade-wind cumuli observed over the Lesser Antilles in the region of the RICO measurement campaign have been made initially. In this very clean air, sea salt and DMS are found to have greater effects than anthropogenic pollution on the warm cloud droplets’ effective radii and longwave and shortwave outgoing top of atmosphere radiation. The changes in radiation due to each aerosol source are a function of how the aerosol particles influence aerosol concentration, cloud droplet number concentration, cloud droplet sizes, and water vapor concentration. These changes are independent of precipitation effects as there is essentially no drizzle in the domain. Simulations show that changes in outgoing shortwave radiation are due predominantly to changes in the clouds, followed by changes in the concentration of the particles (the direct aerosol effect) which has 2/3 the significance of the clouds. The radiative effect due to changes in the amount of water vapor in the atmosphere is in turn about 2/3 as important as the direct effect. Changes in outgoing longwave radiation are due predominantly to changes in the clouds, with changes in water vapor being about 1/10 as important. The simulated changes in water vapor concentration are due to the competing effects of aerosol particles being able to both enhance condensation of available water vapor and enhance evaporation of smaller droplets.

Mixed-phase Arctic Clouds

The next goal of the project is to study aerosol-cloud-water vapor feedbacks in ice-containing clouds. To this end, ice nucleation processes must be incorporated into WRF-Chem, and an ice nucleation parametrization scheme developed for the CAM model has been implemented in WRF-Chem. This scheme relates ice nucleation with the number of aerosol particles available for nucleation, temperature, and updraft velocity– the same atmospheric properties that the activation of liquid cloud droplets depends on. The physical processes included in the ice nucleation scheme are the homogeneous freezing of sulfate, contact freezing on dust, and the immersion freezing of and deposition nucleation on soot, dust, and organic particles. Mixed-phase clouds can exist between 0 -37°C, below which temperature there is no deposition nucleation. The ice nucleation scheme in WRF-Chem is now being tested. When the model is stable, it will be used to simulate mixed-phase clouds observed above Alaska during the ISDAC measurement campaign. When the model is able to reasonably reproduce the observed ice-containing clouds, sensitivity simulations paralleling those performed for the warm clouds described above will be performed. The effects of different types of aerosol particles on arctic mixed-phase clouds and the above-cloud radiation will be compared with the results obtained for the warm clouds. It is expected that the aerosol-cloud-water vapor
interactions will be shown to be more pronounced above the arctic mixed-phase clouds as compared with the warm maritime clouds for several reasons. The reasons include that the arctic mixed-phase clouds exist in a dirtier region with more aerosol particles available (than the exceptionally clean air of the RICO warm-cloud simulations) and in a drier atmosphere where a small change in water vapor can be much more important.
CCN ACTIVITY OF MIXED MODEL-HULIS AND SODIUM CHLORIDE AEROSOL

N. L. Prisle¹, T. B. Kristensen², B. Molgaard¹, M. Bilde², M. Dal Maso¹

¹ University of Helsinki, Department of Physics, P.O. Box 48, 00014, University of Helsinki, Finland.
² University of Copenhagen, Department of Chemistry, Universitetsparken 5, 2100 Ø, Copenhagen, Denmark.

Keywords: MARINE AEROSOL, SURFACE ACTIVITY, WATER ACTIVITY, CCN ACTIVITY.

INTRODUCTION

Atmospheric aerosol particles affect Earth’s climate directly through the scattering of sunlight and heat, and indirectly via the formation and properties of clouds. The indirect aerosol effect is still the most poorly constrained among the known factors contributing to global climate change (IPCC, 2007; Hallquist et al., 2009). Clouds and their formation and properties have important impacts on the hydrological cycle, as well as feedbacks to the cryosphere and formation of ice clouds in the atmosphere (Lohmann and Feichter, 2001). The ice nucleation processes have recently become the focus of several new research activities, from both theoretical and experimental approaches (CRAICC, 2011). Clouds in the atmosphere often contain both ice crystals and liquid droplets. In order to separate and describe the ice cloud formation, properties governing warm cloud formation must therefore also be well-constrained.

The cloud condensation nuclei (CCN) properties of aerosol particles are determined by both size and chemical composition. Atmospheric aerosols often contain significant amounts of organic material (Jimenez et al., 2009) and the presence of surface active compounds within the organic fraction has been demonstrated in bulk samples of atmospheric cloud and fog water, and in aqueous extracts of collected atmospheric aerosol samples from a wide variety of sources and environments (Asa-Awuku et al., 2008; Dinar et al., 2006; Kiss et al., 2005; Mochida et al., 2002; Oros and Simoneit, 2000; Facchini et al., 2000, 1999). Surface active molecules (surfactants) concentrate in the surface and can reduce the surface tension of an aqueous solution. We have previously demonstrated, both experimentally and with comprehensive thermodynamic calculations, how these properties can significantly influence the CCN activation of both pure and mixed aerosol comprising a number of atmospheric organic surfactants (Prisle et al., 2010, 2008, and references therein).

The indirect climate effect of atmospheric particles is particularly important over the Earth’s oceans, due to the large relative change in albedo, from that of the uncovered sea surface, upon formation of clouds. In addition to sea salt (sodium chloride), marine aerosol particles can contain significant fractions of organics (O’Dowd et al., 2004), some of which has been shown to be Humic-like substances (HULIS) (Cavalli et al., 2004). HULIS is a complex mixture of chemically unresolved organic material, which is believed to have significant CCN potential (Krivácsy et al., 2008; Graber and Rudich, 2006). For the sake of both availability and reproducibility of the characterization, reference humic substances have been widely used as model substances for atmospheric HULIS (Fors et al., 2010; Ziese et al., 2008; Wex et al., 2007; Dinar et al., 2006; Gysel et al., 2004; Chan and Chan, 2003). Commonly used references, or model-hulis, for atmospheric organic aerosol are Suwannee River Fulvic Acid (SRFA) and Nordic Aquatic Fulvic Acid (NAFA). It has been a matter
of some debate, which of these commercially available references more closely resembles the properties of real atmospheric HULIS. However, it has been demonstrated that NAFA is more hygroscopic (Chan and Chan, 2003) and reduces surface tension of bulk aqueous solutions more efficiently (Kiss et al., 2005) than SRFA.

In this work, we have aimed to investigate the synergetic effects of surface active model-HULIS and sea salt on mixed organic–inorganic aerosol CCN activity. Previous work on mixed surfactant and sea salt marine aerosol model systems have demonstrated that surface activity influences CCN activation as described in Köhler theory (Köhler, 1936) via both Raoult and Kelvin effects on droplet equilibrium water vapor pressure (Prisle et al., 2010, and references therein). We have therefore chosen to use NAFA as model-HULIS for this work, in order to facilitate the study of the effects of these different properties on mixed HULIS and sea salt particle CCN activity, as well as our ability to properly model their respective contributions.

METHODS

We have measured the CCN activation of mixed Nordic Aquatic Fulvic Acid Reference (NAFA; IHSS:1R105F) and sodium chloride (NaCl; >99.5%, Sigma–Aldrich) particles of different dry sizes (15–120 nm in diameter) and component mixing ratios (0, 20, 50, 80, 100 mass% NAFA). Measurements were made in the water supersaturation range 0.2–2.0% with a continuous-flow cloud condensation nucleus counter (DMT-CCNC) and critical supersaturations were determined from the measured activation curves as described by Moore et al. (2010). The experimental set-up and procedures are otherwise analogous to those described in previous work (Prisle et al., 2010, 2008, and references therein).

In addition, concentration-dependent surface tension and osmolality were measured for bulk solutions prepared with NAFA and NaCl solute mixing ratios corresponding to those of the investigated aerosol particles. Surface tensions were measured with an FTA 125 pendant drop tensiometer. Measurements of osmolality were made on hanging droplets using a Knauer 7000 osmometer. From the measured osmolalities ($C_{\text{osm}}$), solution water activities can be derived with high accuracy according to the relation

$$a_w = \frac{1000}{1000 + C_{\text{osm}}}$$

where $C_{\text{osm}}$ is given in units of Osmoles per kg (of water), and $M_w$ is the molar mass of water (Kiss and Hansson, 2004). Measured surface tensions and osmolality-derived water activities were then used to obtain continuous ternary parametrizations for each property, with respect to the aerosol water–NAFA–NaCl mixing state.

Employing the obtained continuous surface tension and water activity parametrizations, critical supersaturations ($SS/[100\%] = S - 1$) for the investigated particle sizes and compositions were calculated from Köhler theory, by iterating the maximum of the Köhler curves:

$$S = \frac{p_w}{p_w^0} = a_w \exp\left(\frac{4\nu_w\sigma}{RTd}\right)$$

Here, $S$ is the equilibrium water vapor saturation ratio over a spherical droplet, $d$ is the droplet diameter, $p_w$ is the equilibrium partial pressure of water over the droplet, $p_w^0$ is the saturation vapor pressure over a flat surface of pure water, $a_w$ is the droplet water activity, $\nu_w$ is the partial molar volume of water in the solution, $\sigma$ is the droplet surface tension, $R$ is the universal gas constant, and $T$ is the temperature (in Kelvins).

To investigate the effect of NAFA surface activity on the respective Raoul and Kelvin terms of activating droplet, calculations were made with four different representations (Prisle et al., 2011, 2010, 2008, and references therein):
• Surface tension in activating droplets is reduced according to the total NAFA and NaCl concentrations, as given by the ternary surface tension parametrization (1).

• Comprehensive partitioning description (Prisle et al., 2010), where the partitioning equilibrium is iterated together with both surface tension and water activity for each growing droplet size (2).

• Simplified partitioning parameterization (Prisle et al., 2011), where NAFA is assumed to be completely partitioned to the droplet surface, such that NAFA mass in the dry particles has no effect on either concentration or surface tension of the activating droplets (3).

• Traditional equilibrium Köhler theory (Köhler, 1936), disregarding NAFA surface partitioning and assuming the constant surface tension of pure water for all droplet sizes (4).

Table 1 summarizes the account for the different effects of NAFA surface activity employed in each of the respective calculation approaches.

Table 1: Properties included in the different theoretical calculations for CCN activity: bulk-surface partitioning (B/S), concentration dependent surface tension ($\sigma$), and concentration dependent water activity ($a_w$).

<table>
<thead>
<tr>
<th>B/S</th>
<th>$\sigma$</th>
<th>$a_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) macroscopic solution</td>
<td>-</td>
<td>x</td>
</tr>
<tr>
<td>(2) comprehensive model (Prisle et al., 2010)</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>(3) simple partitioning (Prisle et al., 2011)</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>(4) traditional Köhler</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Effects of particle chemical composition on droplet equilibrium growth and activation can be described by the hygroscopicity parameter $\kappa$ (Petters and Kreidenweis, 2007) according to

$$a_w = \frac{d^3 - D_p^3}{d^3 - D_p^3(1 - \kappa)}$$

where $D_p$ is the dry particle diameter and, as before, $a_w$ is the droplet water activity, and $d$ is the droplet diameter. We have investigated the applicability of the simple Zdanovskii-Stokes-Robinson (ZSR) mixing rule (Stokes and Robinson, 1966) to estimating the overall mixed NAFA–NaCl particle hygroscopicity. This was achieved by fitting the measured critical supersaturations ($SS$) for each dry particle composition as functions of particle diameter ($D_p$) to curves described by a single $\kappa$-value. If the droplet surface tension is formally assumed to be that of pure water, the effective $\kappa$-value thus determined can be considered to account for all chemical effects of the particle components on droplet activation, including those related to NAFA surface activity.

$\kappa$-values were obtained from a least-squares fit to Equation 2, using the water activity expression in Equation 3 and assuming a temperature of $T = 298$ K and a surface tension for pure water of $\sigma_w = 72.8$ mN/m. These values obtained directly by fitting measured critical supersaturations were compared to the corresponding values calculated for the same particles by volume-weighted addition of the pure component $\kappa$-values (Petters and Kreidenweis, 2007). Application of volume additivity requires an assumption about the mass density ($\rho$) of pure NAFA. Here, we have calculated additive $\kappa$-values for assumed $\rho_{NAFA} = 1.0$ and 1.5 g/cm$^3$.

CONCLUSIONS

The measured CCN activity for mixed NAFA–NaCl particles decreases with increasing mass fraction of NAFA, for all particle sizes investigated in this work. Thus, varying the dry particle composition
from pure NaCl to pure NAFA, the effect of decreased surface tension at the point of droplet activation, due to presence of surface active NAFA, cannot overcome the simultaneous decrease in solute effect, from the higher molecular mass of pure NAFA, compared to pure NaCl. This was also observed by Prisle et al. (2010) for other marine aerosol model systems, comprising atmospheric fatty acid surfactants and sea salt in various mixing ratios.

By directly measuring ternary aqueous solution surface tension and osmolality for different NAFA–NaCl solute mixing ratios and total concentrations, and subsequently obtaining continuous ternary parametrizations, we were able to calculate mixed particle CCN activity using a detailed thermodynamic model accounting for the synergetic effects of organic–inorganic solute interactions in activating droplets. We applied different representations of the effects of NAFA surface activity in the calculations, to investigate the relative contributions of these effects on overall mixed particle CCN activity. Due to the droplet sizes concerned, the effects of these properties cannot be measured independently for activating droplets, with any currently available techniques. We saw that the overall effect of including surface partitioning is to greatly decrease the CCN activity of surface active NAFA, and the influence of surface activity on CCN activation is evidently more significant in increasing the Raoult term, than on decreasing the Kelvin term. This confirms the previous conclusions of Prisle et al. (2010) for mixed fatty acid salt and sea salt particles.

The CCN activity of the investigated particles is well described by a single $\kappa$-value over the measured size range, for each dry particle composition. For pure NAFA particles, the fitted $\kappa$-value is comparable to those found in other studies of NAFA and SRFA model-HULIS hygroscopicity, and also consistent with $\kappa$-values determined for marine aerosol. Mixed-particle $\kappa$-values estimated from simple volume-weighted addition of the respective pure NAFA and NaCl values are overall comparable to those derived directly from fitting the measured critical supersaturations. Nevertheless, there are deviations between the $\kappa$-values from these different approaches indicating that the ZSR mixing rule does not strictly apply. In particular, these deviations cannot be resolved for the whole investigated range of dry particles sizes by simply changing the assumption of NAFA mass density. There therefore appears to be both size and composition dependencies of the mixed NAFA–NaCl $\kappa$-values that are not captured by simple addition of the pure component $\kappa$-values.

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IN THE FRINGES OF CRYOSPHERE: VOC EMISSIONS FROM HIGH LATITUDE ECOSYSTEMS

P. RANTALA\textsuperscript{1}, T.M. RUUSKANEN\textsuperscript{1}, J. AALTO\textsuperscript{2}, J. BÄCK\textsuperscript{2}, S. HAAPANALA\textsuperscript{1}, H. HAKOLA\textsuperscript{3}, M.K. KAJOS\textsuperscript{1}, J. PATOKOSKI\textsuperscript{1}, S. SCHALLHART\textsuperscript{1}, R. TAIPALE\textsuperscript{1} and J. RINNE\textsuperscript{1}

\textsuperscript{1} Division of Atmospheric Sciences, Department of Physics, University of Helsinki, Finland. 
\textsuperscript{2} Department of Forest Sciences, University of Helsinki, Finland. 
\textsuperscript{3} Air Quality Research, Finnish Meteorological Institute.

Keywords: VOC, PTR-MS, Hyytiälä, winter.

INTRODUCTION

Volatile organic compounds (VOCs) are mostly emitted into atmosphere from natural sources (Guenther et al., 1995). Some of the compounds, such as monoterpenes, are highly reactive and seem to have major contributions to aerosol particle formation and growth, thus these compounds are also connected to the global climate change (Kulmala et al., 2004). Approximately 50\% of the biogenic emissions is coming from the tropical rain forests, 15-20\% from the boreal forests and the rest from the other sources like fields and oceans.

The majority of the biogenic VOC emissions are seasonal dependent and boom after snow melt and at the start of the growing season. Similarly the emissions decline as the weather cools down and senescence of leaves starts in the autumn. In addition, snow and ice cover hinder or inhibit the release of these compounds from oceans, soil and passive pools such as leave and needle litter on the ground. Therefore the changes in periods of snow and ice cover and growing season affect largely the emissions of VOCs.

We have studied VOC-concentrations as well as fluxes using proton-transfer-reaction mass spectrometry (PTR-MS, Lindinger et al., 1998) in Hyytiälä at SMEAR II station (61° 51’ N, 24° 17’ E, 180 m a.m.s.l.) since 2005. We have also measured VOC emissions from vegetation in sub-arctic and permafrost areas, for example from mountain birch at Abisko, Lapland, Sweden (Haapanala et al., 2009), from wetlands in Lapland, Finland (Haapanala, 2006) and from Dahurian larch at Spasskaja Pad flux measurement station, Siberia, Russia (Kajos et al., 2011).

Hyytiälä represents a typical boreal region with clear snow covered winters: annual average temperature has been approximately 3.3°C and the thermal winter (average day temperature below 0°C) stretches typically from November till March. In future, changes in climate could mean winters with shorter snow coverage and longer growing season. This would change the biogenic VOC emissions.

In this work, we present PTR-MS concentration and flux measurements from SMEAR II during cold seasons as a test case in arctic and subarctic regions.

METHODS

The PTR is a highly sensitive technique for online measurements of VOCs. PTR uses hydronium ions (H\textsubscript{3}O\textsuperscript{+}) to ionize target compounds via proton transfer reaction and quadrupole (PTR-MS) or time-of-light (PTR-TOF-MS) technique as a mass analyzer. PTR-MS measures with 1 amu (atomic mass unit) resolution while PTR-TOF-MS has a high enough mass resolution to determine
the chemical composition of the protonated VOCs, however neither identifies isobaric compounds. PTR technique is still the best way to measure major part of VOCs, like methanol, acetone, isoprene and monoterpenes.

Figure 1: Typical measurement setups at SMEAR II station. The figure 1a has been adapted from Ruuskanen (2009).

Our most common used measurement setup at SMEAR II can be seen in figure 1a. Gases are transported from the 22 m high tower to the measurement cabin and the PTR-MS. An acoustic anemometer is used for flux measurements and it is located as near as possible to the inlet line. The fluxes have been measured mostly using disjunct eddy covariance -technique (DEC, see Taipale, 2011) and PTR-MS but some unpublished experiments have been done using surface layer gradient method. However, the gradient technique requires vertical profile measurements above the forest canopy and a little different measurement setup was shown in figure 1a (see figure 1b). We have also used PTR-MS for chamber flux measurements (see figure 1a and Ruuskanen et al., 2005).

The vertical turbulent VOC flux $F$ is, by definition, the covariance between vertical wind speed $w$ and VOC concentration $c$:

$$F = \overline{c'w'} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} w'(t)c'(t) \, dt,$$

where $w'(t) = w(t) - \bar{w}$, $c'(t) = c(t) - \bar{c}$ and $t_2 - t_1$ the flux averaging time. In DEC-method, the time integral (1) is calculated using a discrete sum:

$$F = \frac{1}{n} \sum_{i=1}^{n} w'(i)c'(i),$$
where \( n \) is the number of measurements during the flux averaging time. The DEC-method is a direct way to measure fluxes but it requires a fast response anemometer and gas analyzer. In addition, surface layer turbulence needs to be strong enough that DEC-method can be used properly, therefore, calm nights are usually problematic for DEC-measurements.

The gradient method is a traditional way to measure fluxes and it is based on the parametrization of the surface layer turbulence and first order closure. It means that the turbulent transport and the molecular transport are assumed to be similar and therefore the vertical turbulent flux term \( c'w' \) can be determined in a form

\[
\overline{c'w'} = -K_h \frac{\partial \overline{c}}{\partial z},
\]

where \( K_h \) is a turbulent transfer coefficient for heat and \( c \) is a concentration. \( K_h \) can be determined using Monin-Obukhov similarity theory. Using equation (3) and concentration profile measurements, it is possible to calculate the fluxes without any fast response instruments. However, the gradient method has several requirements (such as a strong horizontal homogeneity) for the measurement site. (see e.g. Foken, 2006)

We started our measurements at the beginning of March in 2011, and the PTR-MS was measuring 27 different compounds from six different measurement levels of the 73 m high tower. Two of the measurement levels (4.2 m and 8.4 m) were below the canopy and four of them (16.8 m, 33.6 m, 50.4 m and 67.2 m) above the canopy (see figure 1b). The calibrations were done using a VOC gas standard. The calibration and volume mixing ratio calculation procedures have been described by Taipale et al. (2008).

The fluxes were calculated using the profile measurements and the gradient method (see e.g. Rinne et al., 2000). Due to tall canopy height (approximately 18 m in spring 2011), roughness sublayer corrections were made for the flux calculations using a method by Rinne et al. (2000).

The average daily temperatures were mostly below 0°C in March and the surrounding areas were covered by snow. Therefore, detected concentrations were extremely low in March and it was very difficult to observe any VOC fluxes (see figures 2 and 4). In April, concentrations were already much larger (see figure 3) and a positive cumulative flux was observed for protonated masses (atomic mass per charge units) 33, 59, 81 and 137 which are assumed to be related to the compounds methanol, acetone, monoterpenic fragments and monoterpenes respectively (see figure 5).

**FUTURE ASPECTS**

We will study the effect of the cryosphere on biogenic sources of VOCs in continuous long term measurements of concentrations and fluxes at SMEAR II with year-round measurements that extend over the snow cover period. This gives us an opportunity to catch, in addition to the capping effect of snow cover over the litter VOC pool emission, the effects of freezing and thawing on vegetation in the autumn and spring. Special emphasis will be on spring, the season with highest aerosol formation events in SMEAR II (Dal Maso et al., 2005) as well as the period when snow melts, growing season starts and VOC emissions increase. Other interest include determining the VOC fluxes of arctic vegetations, including lakes and peatlands.
Figure 2: Concentration of monoterpenes (protonated mass 137 amu) at levels 16.8 m (blue line) and 67.2 m (black line) during 22.3.-26.3.2011. Concentrations are very low and vertical concentration gradient is close to zero.

Figure 3: Concentration of monoterpenes (protonated mass 137 amu) at levels 16.8 m (blue line) and 67.2 m (black line) during 13.4.-17.4.2011. Concentrations are much larger than ca. 20 days before and the gradient is also very clear and negative almost all the time.
Figure 4: Temperature and cumulative flux of monoterpenes (protonated mass 137 amu) during 22.3.-26.3.2011

Figure 5: Temperature and cumulative flux of monoterpenes (protonated mass 137 amu) during 13.4.-17.4.2011
REFERENCES


CLOUD CONDENSATION NUCLEI CLOSURE STUDIES IN THE HIGH ARCTIC

S. SJOGREN\(^1\), E. FORS\(^1\), J. RISSLER\(^3\), B. SVENNINGSSON\(^1\), E. SWIETLICKI\(^1\), M. MARTIN\(^2\), B. SIERAU\(^2\) and C. LECK\(^3\)

\(^1\) Division of Nuclear Physics, Lund University, Lund, Sweden.
\(^2\) Institute for Atmospheric and Climate Science, ETH Zurich, Zurich, Switzerland.
\(^3\) Department of Meteorology, Stockholm University, Sweden.

Keywords: AEROSOL-CLOUD INTERACTIONS, AMS, HTDMA, CCNC.

INTRODUCTION

The radiative balance between incoming shortwave solar radiation and outgoing longwave radiation to a large extent determines the warming of the Arctic and the fate of its cryosphere. Clouds play a major role in this balance. For cloud formation, aerosol particles are necessary (Ristovski, 2009). Due to logistical constraints, measurements of relevant aerosol particle properties and the particle interactions with cloud droplets in the high Arctic are rare. Here, we present results from icebreaker expeditions to the summer high Arctic where we examine to what extent the physical properties of the Arctic boundary layer aerosol can be used to account for the cloud-nucleating properties of the same aerosol, by comparing with parallel measurements of the concentration of cloud condensation nuclei (CCN). The most recent CCN closure study was based on measurements that were carried out in August 2008 during the IPY-approved Arctic Summer Cloud Ocean Study (www.ascos.se) on board the Swedish icebreaker Oden. The main data were collected during a three-week period in the pack ice region (> 85° N) when the icebreaker Oden was moored to an ice floe and drifted passively with the trans-polar current. Measurements were performed during a biological active period and into autumn freeze up conditions. We compare the results from ASCOS 2008 with similar CCN closure studies from the two previous icebreaker expeditions to the same region; AOE-2001 in July-August 2001 and AOE-96 in 1996 (Leck et al., 2004; Zhou et al., 2001).

METHODS

During ASCOS 2008, CCN number concentrations were obtained using two CCN counters (DMT, USA), measuring at various water vapour supersaturations. One was scanning over different supersaturations (SS, namely 0.1; 0.15; 0.2; 0.41 and 0.73 %SS), one measured at a constant SS (0.17 %SS until Aug. 16th, then 0.22 %SS). Both instruments compared well throughout the campaign at the relevant SS. Two differential mobility particle sizers (DMPS) were used to measure the aerosol dry size distribution. In this study all particle sizes indicated are diameters. The relevant dry particle size interval used for this study was 0.03 to 1 \(\mu\)m. The directly measured CCN number concentration was first compared with the CCN number concentration predicted using bulk aerosol mass composition data from an aerosol mass spectrometer (Aerodyne c-ToF AMS) and the DMPS aerosol size distributions, assuming Koehler theory and an internally mixed aerosol (Martin et al., 2011). The AMS had a minimum dry particle cut-off diameter of about 70 nm, thus not capturing the chemistry of the smallest particles activated at the highest supersaturation settings. The AMS had a time resolution of 5 minutes and did not measure size-resolved data for the totality of the expedition. The AMS normally provides the chemical composition of the submicrometer aerosol
with respect to the major components, which in turn determines the hygroscopic properties. In contrast, a hygroscopic tandem differential mobility analyzer (HTDMA) measures the size-resolved (30-263 nm) hygroscopic behaviour in the subsaturated regime (up to 90% relative humidity), including the extent of internal/external mixing, and with a time resolution of 1 hour. Chemical composition is however not measured directly by the HTDMA, but need to be inferred. In a second approach used in this study, size-resolved measurements of the hygroscopicity (water uptake), from dry size 263 nm down to 30 nm, was used in the closure, instead of the AMS composition. A volatility-TDMA (VHTDMA) also provided additional information.

RESULTS

Closure could be achieved using the mass spectrometry data (“AMS-approach”) at 0.10, 0.15 and 0.20% supersaturation (Martin et al., 2011), for certain assumptions regarding particle density and hygroscopicity of the organic fraction. The best agreement of the predicted CCN number concentration against the measured one was found when the organic fraction of the aerosol was assumed to be nearly insoluble ($\kappa_{org} = 0.02$). However, this is not unambiguous and $\kappa_{org} = 0.2$ is found as an upper limit at 0.1% supersaturation. For the two highest supersaturations, 0.41 and 0.73%, closure could not be achieved with the investigated settings concerning hygroscopicity and density. The predicted CCN number concentration is always higher than the measured one, suggesting that the smaller particles that activate at these supersaturations have a relative larger insoluble and/or organic mass fraction than the larger particles. The HTDMA measured that the hygroscopicity decreases with decreasing size (more than calculated by the Kelvin effect alone), which supports the assumption that the smallest particles contain a larger mass fraction of organics relative to the larger (accumulation mode) particles.

An overview of the closures from the different expeditions, using HTDMA data, is shown in Figure 1. It is observed that the 2008 and 1996 closures are similar, and the model overpredicts the CCN concentration measured with about 40%. For the 2008 expedition the average of the ice-drift period is shown, for the 1996 expedition data from throughout the entire expedition. An overprediction of about 40% is on the upper end of what is generally reported in literature for lower latitudes around the globe (Kammermann et al., 2010). The variability over time during an expedition is noticeable, which will be detailed below for the 2008 expedition, and reflects in the correlation parameter $R^2$ which is quite low, around 0.7. The 2001 expedition data results in a closure with ratios of predicted to measured CCN concentrations around 1. This indicates an annual variability in aerosol properties which is of similar order as what is possible to resolve considering the instrumental errors.

<table>
<thead>
<tr>
<th>Period</th>
<th>Start time</th>
<th>End time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>August 14 18:00</td>
<td>August 16 08:00</td>
</tr>
<tr>
<td>2</td>
<td>August 17 02:00</td>
<td>August 19 16:00</td>
</tr>
<tr>
<td>3 &quot;Pre-freeze&quot;</td>
<td>August 21 03:00</td>
<td>August 23 02:00</td>
</tr>
<tr>
<td>4</td>
<td>August 27 01:00</td>
<td>August 30 11:00</td>
</tr>
<tr>
<td>5 &quot;Freeze-up&quot;</td>
<td>August 30 13:00</td>
<td>September 2 04:00</td>
</tr>
</tbody>
</table>

Table 1: Periods defined for the ASCOS project with constant meteorological and trajectory patterns.

Two time periods from the 2008 expedition (Period 4 and 5 from Table 1) were selected (out of currently five defined), based on meteorological parameters, trajectory analysis and aerosol properties. The closure results calculated using HTDMA data and the same DMPS data used for the Martin et al (2011) closure study is shown in Figure 2 (“HTDMA approach”). Data for period
Figure 1: Closure performances as a function of SS of different CCN activation closure studies. Sizes of symbols are proportional to $R^2$ of the correlations. The error bar uses the same assumptions as in (Fors et al., 2011), and is similar for all expeditions.

4 was extended back to the end of period 3, without influencing the CCN closure, in this case. The last closure point during period 4 was August 29th 2008 at 10:00 (due to a lack of fitted HTDMA data due to very low concentrations the next 24 h - perhaps this can be overcome with a more detailed study). All times indicated are UTC.

It is observed that, for period 5, the CCN activation model (Rissler et al., 2004) overpredicts the CCN concentrations when compared to those measured by the CCN counter with 20%. This is significantly lower than the average for the expedition. The 50% overprediction of CCN concentrations for period 4 is significantly higher. The result is similar for other supersaturations. This is beyond the largest propagated errors, which provokes such questions as: i) what was the difference in aerosol properties between the two periods, and; ii) what processes can control the activation such that the critical supersaturation is that much higher relative to the measured subsaturated water uptake?

Period 4 is characterized by relatively warm ambient temperatures (-3 to -1 °C) and cloudy conditions. Cloudiness is preliminary assessed from visibility, ceilometer, cloud radar, ambient RH, FSSP, all-sky imager and photos. From August 28th 2008 at 14:00 the footprint (Flexpart, by A. Stohl, ASCOS database) is significantly enlarged and begins to cover a wider area of most of the Arctic Ocean basin, with possible influence from widespread anthropogenic sources at lower latitudes, although they would be diluted at arrival to site. The $^{210}$Pb activity concentrations (Paateto et al., 2009) reach the highest value recorded, 110 $\mu$Bq m$^{-3}$, as an average during August 28th. During August 31st, the daily average falls below the detection limit of 5 $\mu$Bq m$^{-3}$, in contrast. This reduction is not entirely due to less air mass land contact, but also due to the low concentrations of the accumulation mode aerosol onwards. Until 10:00 on the 30th of August, a weather system with a cloud structure at an altitude of 4 to 8 km prevailed. The FLEXPART
model calculates an aerosol footprint partly from northernmost Canada until then. After this time until the departure of Oden (Sep. 2nd, 00:00), the footprint is consistently from over the arctic pack ice. The HYSPLIT model calculates similar results, and further, indicates during the 31st that air masses at altitude 800 m subside from 1500 m (48 hrs earlier), in contrast to before the 31st, where the air masses origin from lower or similar altitudes (48 hrs earlier). This indicates more possibilities for mixing down to surface during Period 4 and more fair weather developing during Period 5.

Period 5 is characterized by freeze-up. With ambient temperatures down to -13 °C, also the larger open leads freeze over. The wind direction was northerly, changing slowly to east the 31st -1st. Wind speed was lower, 2-4 m s⁻¹. The air mass history is from Western Central Arctic Ocean. The 31st of August was a day with fog/clouds from 06:00 until about 10:00 (from groundlevel up to about 1 km) and afterwards it was clearing up. The particle concentration measured in the lab was low, and total number concentrations varied between 0-100 cm⁻³ (similar concentrations as the preceding 24 h). During September 1st the weather was fair with good visibility from midnight until 9:00, when fog developed and prevailed until about 17:00. Then a new particle formation (NPF) event occurred where 4 nm nucleation mode particles became numerous (1000 cm⁻³), increasing in size with 0.5 nm h⁻¹.

In summary, the conditions that differ between Period 4 and 5 were thus the cloudiness and thus the amount of shortwave radiation reaching the arctic boundary layer (ABL). Period 5 was predominantly sunny. The air masses for each period was influenced by lower latitudes and pristine Arctic, for Period 4 and 5, respectively. Heinzenberg et al. (2006) hypothesizes that fog processing can have an influence on the aerosol properties. We have not yet repeated that analysis algorithm with this data, but there is nothing apparent that does contradict their finding currently. Leck et al. (2002) have observed underprediction during sunny conditions, and overprediction during cloudy which is similar to the current observations in period 5 resp. 4. It appears as if the HTDMA approach closure is closer to 1 for the air masses such as encountered during Period 5, which has been observed during former expeditions (at times such conditions result in an underprediction, see Lohmann and Leck (2005), albeit with a different approach to estimate the CCN concentration).
Processes that can explain an overprediction, which was more pronounced during Period 4, are: surface tension (increasing surface tension with increasing water uptake in HTDMA from 90 %RH to the point of activation), surface partitioning (Sorjamaa et al., 2004), volatility issues (rather an instrumental artifact) and possibly a stronger separation of condensable species onto the aerosol in the Arctic atmosphere, more than what is occurring at lower latitudes. Future work will investigate these issues.

CONCLUSIONS

Two CCN closures, one from chemistry data and from one HTDMA data, have been performed, for the ASCOS 2008 expedition in the High Arctic. The two closures show similar tendencies, however on at least two occasions of periods of days they differ. This gives good information on the nature of the aerosol and measurements during typical Arctic conditions. First, when concentrations are low the AMS can underestimate the organics, resulting in an overprediction (e.g. Period 5). Secondly, as AMS does not discern some features of the aerosol, such as water uptake of smaller particles than diameter 70 nm and external mixture, for higher supersaturations than 0.25% the closure become less certain. Thus HTDMA measurements is an important complement. In despite of using the HTDMA information a period remains where the chemistry closure underpredicts and the HTDMA closure overpredicts the CCN number concentration (e.g. August 25th). This will be further investigated.

The pronounced overprediction we observed in the ASCOS data shows that the Kohler model alone cannot be used to achieve closure for all investigated cases. We suggest to add the following two considerations how to extend the applied model for the calculation of the CCN number concentration: i) increasing surface tension at activation (preliminary results show up to 5% change in CCN concentration predicted at 0.73% SS) ii) surface partitioning (examples in literature show a non-negligible influence on specific systems).

We conclude that, in general, a prediction of CCN concentration based on chemistry or HTDMA data is feasible, however, with marginally larger uncertainty than at lower latitudes. Details related to the theoretical calculation of the CCN concentrations remain to be solved. Herein, the uncertainty in the CCN closure, in contrast, could have also been influenced by the measurement location/environmental conditions that affect CCN properties and in turn their experimental determination. In this remote location, the air parcel history or the prevailing meteorological conditions might influence the CCN properties more consistently over time compared to at lower latitudes, perhaps resulting in less homogeneous aerosol properties, for instance a more distinct morphology.

ACKNOWLEDGEMENTS

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A HEMISPHERIC DATA SET OF TREE SPECIES FOR USE IN AEROSOL SCIENCES

C.A.SKJØTH¹,², H.SKOV² and A.MASSLING²

¹Department of Earth and Ecosystem Sciences
Division of Physical Geography and Ecosystems Analysis
Lund University
Sölvegatan 12, 223 62 Lund, Sweden

²Faculty of Science and Technology, Department for Environmental Science,
Aarhus University, P.O.Box 358, Frederiksbergvej 399,
4000 Roskilde, Denmark

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INTRODUCTION

Forests act as an important source of gasses and particles to the atmosphere. Detailed data on e.g. tree species of forests and their capability to release gasses (e.g. precursors of aerosols) and aerosols is therefore relevant in the context of atmospheric science. For some gas and aerosol emissions, the distribution of trees down to genus or species level is critical. The release of Volatile Organic Compounds (VOC’s) (Dindorf et al., 2006; Guenther et al., 2006) is an important example of such emissions, since the distribution of VOC species and the emission strengths varies strongly between species (Simpson et al., 1999). Similar figures have been presented for allergenic pollen (Belmonte et al., 2008; Hernandez-Ceballos et al., 2011; Skjøth et al., 2007; Skjøth et al., 2009; Sofiev et al., 2006). From several research projects it has been concluded that the location of the source is one of the most critical information with respect to this allergenic aerosols originated from the biosphere (Sofiev et al., 2006; Zink et al., 2011) – which unfortunately is often highly unknown. Dynamic Vegetation Models can be used to describe the evolution of forest cover, the important feed-back processes between the biosphere and the climate system (Jones et al., 2009) as well as the release of VOCs such as isoprene and terpenes to the atmosphere (Arnth et al., 2011). However, many processes in relation to isoprene production are still poorly understood and it has also been shown that these Dynamic Vegetation Models are sensitive to underlying vegetation fields. Improvement of vegetation fields including forest cover on species level is therefore highly relevant to atmospheric science. Recent studies have suggested simple methods for improving vegetation fields with respect to forest cover on species level (Skjøth et al., 2008). However, these studies were limited with respect to geographical coverage as they did only cover Europe. They were therefore of limited use for large scale studies such as studies focusing on areas outside Europe such as Russia or Canada. The aim of this presentation is to investigate if the method by Skjøth et al. (2008) can be applied on larger scales such as Euroasia and North America by studying the reported densities of birch trees among forests on the Northern Hemisphere.

METHODS

Statistical data on birch tree density in broadleaved forests were obtained from each country in Europe, Russia and Canada. Three different sources for data are considered: Canadian Forest Inventory, the data base by Skjøth et al. (2008) and a data base for the Russian Forest fund (Isaev and Shvidenko, 2002). We use the same methodology and approach as in Skjøth et al (2008) in order to harmonize and investigate the data with respect to species coverage. Statistical data on species level in forests are available for 13 regions in Canada, 138 in Russia and 765 in Europe (excluding Russia).

First results show that data are available within the entire region of interest. The Euroasian region has a much higher density of birch trees compared to Canada. Contrary, Canada has a much higher density of poplar and aspen (not shown). Several regions have however also a very large percentage of undefined tree species.
CONCLUSIONS

Inventorying tree species in forests on sub-national level seems absolutely possible and promising as for all regions data are available. However it is also evident that additional information from non-forest inventories needs to be taken into account and a large amount of resources has to be provided concerning the harmonization before a usable database can be presented, regridded and combined with remote sensing data such as the Global Land Cover data set (Hansen et al., 2000).
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ESTIMATED CHANGES IN HIGH LATITUDE EMISSIONS OF SEA SALT AEROSOL IN THE PAST AND FUTURE CLIMATE

H. STRUTHERS¹,²,³, J. ZÁBORI¹, E. D. NILSSON¹, R. KREJCI¹, E. M. MÅRTENSSON¹,⁴, AND A. M. L. EKMAN²,³

¹ Department of Applied Environmental Science, Stockholm University, Stockholm, SE-11418, Sweden.
² Department of Meteorology, Stockholm University, Stockholm, SE-10691, Sweden.
³ Bert Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden.
⁴ Department of Earth Sciences, Uppsala University, SE-752 36 Uppsala, Sweden.

Keywords: Marine aerosols, sea salt, Climate, Polar regions, Emissions

INTRODUCTION

Sea salt aerosol contributes significantly to the global aerosol particle burden and radiative budget, and may be the dominant contributor to light scattering and an important source of cloud condensation nuclei (CCN) in remote marine areas. In the Arctic, a feedback mechanism whereby changes in Arctic sea ice influences aerosol particle number emission and composition which in turn affects the radiative balance and climate forcing has been proposed. How this feedback mechanism may impact cloud microphysics in the Arctic remains unclear (Struthers et al., 2011).

The main physical driver of sea salt emissions is the near-surface wind speed (U₁₀) with emissions being regulated by the sea ice cover in the polar regions (Nilsson et al., 2001). In-situ measurements also show that sea spray emissions are reduced to an insignificant level by the presence of sea ice (Nilsson et al., 2001; Held et al., 2011). An increasing number of studies support the conclusion that sea salt aerosol emissions are dependent on the sea surface temperature (SST) (e.g. Hultin et al., 2010). New measurements from Svalbard as part of the GRACE (Green House Arctic Ocean and Climate Effects of Aerosols) project suggest an enhancement of the particle number flux for temperatures lower than 5°C. SST changes have also been found to influence the size distribution of the aerosol emissions (Mårtensson et al., 2003; Hultin et al., 2010; Jeagle et al., 2011; Nilsson et al., 2010) which is important from a climate perspective because the scattering of solar radiation and the formation of cloud droplets are highly dependent on the size of the aerosol particle.

The aim of this study is to examine long-term changes in high latitude emissions of sea salt aerosol by employing a modification of the Mårtensson salt aerosol emission parameterization (Mårtensson et al., 2003) based on the new GRACE in-situ experiments at temperatures near freezing (see Zábori et al., this issue). The new Mårtensson/Zábori source function (MZ11) is combined with climate model output from the World Climate Research Programme’s (WCRP’s) Coupled Model Intercomparison Project Phase 3 (CMIP3) multi-model dataset and the Paleoclimate Modelling Intercomparison Project Phase II (PMIP2) database. This allows us to calculate global emissions over the period 1870-2100, the last glacial maximum (LGM) and the mid-Holocene periods. From these emission estimates, we are able to assess the relative importance of changes in the different drivers of sea salt emissions (U₁₀, SST and sea ice cover) on global and regional scales. The emission calculations may also assist in interpreting ice core measurements of sea salt ions. In addition, the atmospheric oxidation of methane by chlorine radicals has a distinct kinetic isotope signature which
means that long period variations in sea salt aerosol concentrations strongly influence the isotopic fractionation of methane extracted from firn air in ice core samples (Levine et al., 2011).

METHODS

A comparison of the original Mårtensson parameterization (MN03) alongside the MZ11 source function is shown in Figure 1. Also depicted is the source function of Monahan et al. (1986) which is generally recommended for use when $D_p > 2.5 \mu m$. Note, there is no temperature dependence in the Monahan source function.

Figure 1: (a) Original Mårtensson sea salt aerosol source function (MN03) for a range of temperatures. Also shown is the Monahan source function for particle diameters greater than 700nm. (b) The new Mårtensson/Zábori sea salt emission parameterization (MZ11). $U_{10}$ is assumed to be 9 ms$^{-1}$.

MN03 uses a linear relationship to describe the SST dependence of the sea salt aerosol emissions. The new MZ11 source function augments MN03 by adding non-linear terms (up to forth order) for temperatures less than 10°C. This non-linear temperature behaviour was determined through analysis of low temperature experiments performed in Svalbard as part of the GRACE project (Zábori et al. 2011, in preparation). Two slightly different non-linear relationships are used for particles with $D_p < 250$ nm and $D_p > 250$ nm, this cutoff size being determined by the characteristics of the instruments employed in the experimental setup.

Figure 2 compares the temperature dependence of the number emissions for the MZ11 and MN03 integrated over three size ranges (Ultrafine 20nm - 100nm; Accumulation 150nm - 500nm; Coarse 1\mu m - 5\mu m) and the total integrated number emissions from 20nm - 5\mu m (Figure 2d). In all cases the MZ11 function shows higher emissions at low temperatures compared to MN03. Sea salt number emissions are dominated by ultrafine particles (see Figure 1) and so the total integrated emissions (Figure 2d) show a similar temperature response to the ultrafine particles (Figure 2a), with modest differences between MZ11 and MN03 at low temperatures. On the other hand, accumulation and coarse mode particle emissions exhibit greater differences between the two parameterizations. These size ranges can act directly as CCN which means there may be significant implications for aerosol-cloud interactions at high latitudes using the updated source function although inclusion of the new parameterization into a fully coupled climate model is outside the scope of the work presented here.
Figure 2: Integrated number emission fluxes as a function of SST for the three aerosol modes indicated in Figure 1(a) and the full size range (20nm - 5µm). Full lines indicate the MZ11 source function and the dashed lines are calculated using MN03. $U_{10}$ is assumed to be 9 ms$^{-1}$ in all cases.

RESULTS: ARCTIC 1870 - 2100

The time series of integrated emissions (20nm - 5µm), area weighted from 65°N to 90°N are shown in Figure 3 based on output from the c20c3m (climate of the 20th century) and SRESa1b CMIP3 model output for the periods 1870 - 2000 and 2000 - 2100 respectively. Three sets of calculations were performed to determine the sensivity of the Arctic emissions to changes in $U_{10}$, SST and sea ice cover:

- Control: Emissions calculated using the complete MZ11 source function
- SST: SST values held fixed at climatology representative of the year 2000.
- SST-ice: SST and ice cover values held fixed at climatology representative of the year 2000.

Figure 3: 65°N - 90°N area weighted average time series of the change in integrated sea salt number emission fluxes over the particle size range 20nm - 5µm for the three sets of calculations (Control: black, SST: orange and SST-ice: blue).
The difference between the control and the SST and SST-ice emissions provides a measure of the relative importance of changes in SST and sea ice cover on Arctic sea salt aerosol emissions. From Figure 3 it is clear that sea ice cover is the most important parameter for controlling changes in sea salt emissions over the period 1870 - 2100, with changes in SST playing a lesser role. Additional calculations (not shown) indicate that changes in $U_{10}$ are relatively unimportant in determining the change in Arctic sea salt aerosol emissions over this time period.

RESULTS: ARCTIC, LGM, MID-HOLOCENE AND PRESENT DAY

Monthly averaged Arctic sea salt aerosol emissions (area weighted from 65°N to 90°N) are depicted in Figure 4 for the LGM, mid-Holocene and present day, calculated by combining the MZ11 source function with fields from the PMIP2 database. For comparison, the same calculations as described above but using the MN03 source function are also shown in Figure 4 (dashed lines).

Figure 4: 65°N to 90°N area averaged sea salt aerosol emissions (integrated number emissions: 20nm - 5µm) for present day, mid-Holocene and LGM conditions as simulated but the PMIP2 climate models. Solid lines are calculations using the MZ11 sea salt aerosol emission parameterization, whilst the dashed lines are from the MN03 parameterization.

The differences in between the MZ11 and the MN03 parameterizations for the integrated number emissions over the full 20nm - 5µm size range shown here are modest as suggested from Figure 2d. Significant differences between the two parameterizations are found for the accumulation and coarse modes when integrated separately (not shown).

The annual cycle of Arctic emissions is controlled by a combination of $U_{10}$, SST and sea ice cover. Emissions peak in autumn due to stronger wind speeds compared to summer followed by a winter decline in emissions which is related to the seasonal increase in sea ice cover. Changes in all the fields that drive emissions ($U_{10}$, SST, sea ice cover) are evident in the PMIP2 models when comparing present day, mid-Holocene and LGM output. Further analysis will allow us to quantify the sensitivity of the estimated emissions to simulated changes in the forcing fields. In addition, further details of the change in the size distribution of the emissions can be determined which will help inform us on possible high latitude climate feedback processes.

This study also includes sea salt emissions in waters surrounding Antarctica, though not presented here.
CONCLUSIONS

The interplay between $U_{10}$, SST and sea ice cover in determining sea salt aerosol emissions implies that a complex climate feedback mechanism is present in the Arctic climate system which in addition is coupled to other feedbacks (e.g. snow/ice albedo feedback). An improved understanding of the relative importance of the drivers of long-term sea salt aerosol changes assists in disentangling which processes are most important in determining Arctic aerosol-climate feedbacks.

This study shows that for the Arctic, the change in ice cover is the most important physical factor determining changes in sea salt emissions in response to climate change. Second to this is the SST, whilst wind speed appears to have a negligible effect. Of course, the decrease in sea ice is in part a response on changes in SST, as these are closely related. Overall, chyosphere changes in the Arctic have the potential to increase this important natural aerosol source by more than 30% up to 2100, but changes so far are negligible. Considering the present day and mid-Holocene, sea spray emissions appear to have had roughly the same magnitude in the Arctic, whilst LGM emissions are up to a factor two higher, depending on season.

SST influences sea salt emissions not only by changing the total number flux (as is the case with $U_{10}$ and sea ice cover) but also the size distribution of the aerosol flux is altered. Further research is required to determine the implications of this effect on the sea salt aerosol radiative forcing. Future plans include extending this work to study the combination of sea salt and marine organic aerosol emissions.

ACKNOWLEDGEMENTS

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REFERENCES


INTRODUCTION

The life cycle of Black Carbon has been of scientific interest for decades (e.g. Ogren and Charlson, 1983). Since sources typically are co-located with people, for instance emissions from traffic or domestic use of biomass fuel for cocking or heating, health related problems caused by inhaling these combustion particles stress the importance of understanding near field processes. Black Carbon particles are special in that they are strong light absorbers, which make them different to almost all other atmospheric particles. Even in comparatively minute concentrations these particles may be of importance to the radiation budget, both while suspended in air or deposited on snow or ice, which stress the importance of understanding far field processes.

A recent study by Skeie et al. (2011) where calculated concentrations using the Oslo CTM2 model was compared to observations from nine different monitoring stations in the Northern Hemisphere illustrates the difficulties to reproduce the observations. In particular, the strong seasonality of the Arctic Haze phenomenon in spring is poorly captured by the numerical simulations. The discrepancy between model and observation is a measure of our lack of understanding and the need to better understand and describe key processes in the models.

Recently Garrett et al., (2010) addressed the relative importance between precipitation scavenging and transport of pollutants in controlling the seasonal cycle of aerosol loading at Barrow, Alaska, by using carbon monoxide as a passive tracer in order to normalize the data. The authors found that wet removal is key for the seasonal variation of Arctic Haze.

In this study we investigate specifically the relationship between light absorbing particles observed at the Zeppelin station, Svalbard and accumulated precipitation derived from HYSPLIT trajectories. By assuming a fixed boundary layer height, the observed relations can be used to calculate washout ratios, that can be used to compare with other studies.

METHODOLOGY

The approach is very straightforward. Two data sets are used. Firstly, the observed particle light absorption, and secondly, the accumulated precipitation derived from trajectories arriving the measurement location. The two data sets are compared to investigate statistical relationships between precipitation and light absorbing particles.

Measurements of light absorbing particles were performed at the Zeppelin station in Ny-Ålesund, Svalbard (78°54’ N, 11°53’ E). The station is located on a mountain ridge at 475 m altitude. Of a custom built Particle Soot Absorption Photometer (PSAP) is used to measure light absorbing particles.
Ström et al. Observed BC concentrations and calculated precipitation in the Arctic (Krecl et al., 2007). The instrument uses a green LED as a light source and records the transmission of light across a cellulose filter substrate. The rate of change of transmitted light as particles deposit on the filter is a measure of the concentration in the air. Data is corrected for filter effects, amount of loading and for co-deposited light scattering particles (Bond et al., 1999). The primary physical quantity from the measurement is absorption coefficient $\sigma_{abs}$ (m$^{-1}$). Data used in this study are hourly averages spanning from March 2002 to September 2008.

For each hour of the time period investigated, a 240 hour back trajectory was calculated using the HYSPLIT model (ref). The starting point was the location of the Zeppelin station and 500 m altitude. Each $Q_{abs}$ data point was matched with a corresponding trajectory. Precipitation along the trajectory was accumulated to a total precipitation $P$ (mm). No special consideration was taken for the altitude of the trajectory.

Clearly each individual data pair is associated with large uncertainties. The observed $V_{abs}$ as such, but also details about the trajectory. Backwards calculated trajectories that extends over more than a few days are known to be uncertain both with respect to the horizontal and vertical position as well as for meteorological parameters derived from the model. During transport air masses mix and the air parcel that arrive the sampling location actually represents the history of many air parcels. Thus, we view the 10-day trajectories mainly as representative for seasonal transport and precipitation patterns.

RESULTS

Data was initially divided into months of the year. The month with least data is February (1140 data points) and the month with most data points is July (2797 data points). For each month, data was further grouped into 10 bins according to the amount of precipitation, $P$. These groups were, <1, 1-2, 2-4, 4-7, 7-10, 10-15, 15-20, 20-25, 25-30, 30-60 mm. For each group the median $V_{abs}$ and median $P$ was calculated. Data is presented in Figure 1. There is a general trend of decreasing $\sigma_{abs}$ with increasing $P$. For some months, such as August for instance that represents one of the smallest $\sigma_{abs}$ ranges, this is not true. Note that the $\sigma_{abs}$ scales are very different between months, but the tick labels are consistent for reference. The month of September which covers the smallest range in $\sigma_{abs}$ still presents a clear relation between $\sigma_{abs}$ and $P$. Hence, the relation is not only dependent on the $\sigma_{abs}$ signal.

We wish to fit one form of functional dependence between the two variables to be able to compare different months. Given the variation between the months it is difficult to pick one function and objectively fit this using some “least square” method. We selected the simple functional form,

$$\sigma_{abs} = A \frac{1}{(1+P)^b} \quad \text{(eq.1)}$$

Where A (m$^{-1}$) is the amplitude of $\sigma_{abs}$ when $P=0$, and b is the efficiency by which light absorbing particles are removed by the precipitation. In relative terms the scavenging per mm precipitation is more effective for the first mm of precipitation. The two coefficients A and b, where tuned subjectively to make the functional dependence capture the overall trend portrayed by the data points. For most months the results are excellent, where as for January and August it is more mean conditions that are captured by the fitted curve. The numeric values of A and b, and the Pearson correlation coefficient for each month are listed in Table 1.
Table 1. Subjectively fitted parameters for monthly relations between light absorbing particles and precipitation as presented in Figure 1 with a functional dependence as in eq. 1. The correlation coefficient between both $A$ and $b$, present some symmetry between spring and fall with local maxima in March and October. The coefficient $b$, shows an additional smaller enhancement in summer. However, given the subjective curve fitting, details should be taken with caution. The $A$ coefficient can be interpreted as mainly related to transport of light absorption by particles, whereas the $b$ coefficient is related to the scavenging efficiency of light absorbing particles.
ACKNOWLEDGMENT

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REFERENCES


ALCOHOL SURFACTANT EFFECTS ON ATMOSPHERIC PARTICLES

E.S. THOMSON 1, X. KONG1, N. MARKOVIĆ2 and J.B.C PETTERSSON1

1 Department of Chemistry, Atmospheric Science, University of Gothenburg, SE-412 96, Gothenburg, Sweden.
2Department of Chemical and Biological Engineering, Physical Chemistry, Chalmers University of Technology, SE-412 96, Gothenburg, Sweden

Keywords: ADSORPTION, DESORPTION KINETICS, MOLECULAR BEAM, WATER UPTAKE.

INTRODUCTION

In the atmosphere interactions between liquid droplets, ice particles, and other aerosols with gas phase molecules have important physical and chemical effects. Processes from cloud formation to photochemistry can be effected by changes in molecular level kinetics. Surfactants may play an especially important role due to their ability to suppress and/or stimulate adsorption and desorption kinetics of atmospheric particles. Alcohols are a particularly interesting group of surfactants because of their ubiquity and diversity in the atmosphere (Hudson et al., 2002). Alcohol coverages can be important sources or sinks of HOx radicals and may change the hydroscopicity of atmospheric particles (Winkler et al., 2002).

Hydroxyl groups allow alcohols to form hydrogen bonds and for the shortest molecules, like methanol, make them highly miscible in water. As the number of carbon atoms increases the solubility decreases, likely also effecting the compounds surface activity. Using Environmental Molecular Beam (EMB) technology we are able to probe the molecular kinetics of alcohol-water systems under atmospherically relevant conditions. The experimental findings illuminate fundamental material properties and are of importance for the description of the effect of organic compounds on heterogeneous atmospheric processes.

METHODS

The EMB apparatus is an ultra-high vacuum (UHV) system that has been modified with an inner chamber surrounding a substrate surface. Within this chamber finite vapor pressures (10−3 mbar range) can be sustained allowing for the formation of stable alcohol and water layers in dynamic equilibrium with their vapor. The surface layers can be probed using molecular beam and light scattering techniques. The EMB apparatus has been described in detail previously (Andersson et al., 2000; Kong et al., 2011a; Thomson et al., 2011) and differs critically from other UHV systems in that it allows surfaces under atmospherically relevant temperatures and pressures to be directly probed.

Information on kinetics is collected by analyzing molecules desorbing from the surface using a quadrupole mass spectrometer. Typically the incident beam is a combination of He and D2O gases. Elastically scattered helium is used to monitor surface coverage, while the simultaneous use of heavy water allows us to accurately monitor water uptake. The reflections of a 670 nm laser from the surface are monitored as alcohol-water layers evolve. Using a simple theory for the attenuated reflected intensity ratio we calculate film thicknesses and surface structure parameters (Kong et al.,
RESULTS

We have used the described techniques to study systems that include both methanol and butanol. In addition to pure alcohol layers, systems of alcohol covered water ice are investigated. We find that both methanol and butanol have interesting effects on ice and water, but these effects are quite distinct from each other.

Methanol is observed to affect ice surface structure while being a generally permeable layer to water molecules. Pure methanol layers are observed to incorporate water molecules in a temperature dependent fashion (Figure 1) and over ice surfaces do not interfere with ice growth by adsorption. The desorption of water from methanol layers follows Arrhenius type behavior with kinetic parameters indicative of multiple hydrogen bonds (Thomson et al., 2011). One implication is that methanol could actually increase the hydrophilicity of otherwise hydrophobic atmospheric particles.

Contrastingly, butanol and butanol covered ice are much less hydrophilic than methanol. Pure butanol is not observed to incorporate water and on ice it can provide a surface coating that limits the incorporation of water. When butanol is introduced onto layers of water ice, the underlying ice structure is preserved, unlike when methanol is added, initiating structural changes.

DISCUSSION

We have developed methods for investigating the molecular kinetics of water, ice, methanol and butanol at temperatures from 165 K to 235 K. We observe distinct differences in the surfactant behavior of methanol and butanol that may have important implications for heterogeneous atmospheric processes. The techniques we have developed can also be used to quantitatively categorize other atmospherically important compounds. Areas of ongoing investigation include experimental measurements to classify the important time scales of water-alcohol interactions, studies of isotopic
effects, and quantifying effects of varying organic layer coverage.

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REFERENCES


ICE MELTING ARCTIC OCEAN AND CLIMATE: BUBBLE BURST PARTICLES

P. VAATTOVAARA1, J. ZÁBORI2, T. GUSTAFSSON3, A. LAAKSONEN1,4, R. KREJCI2 and D. NILSSON2

1University of Eastern Finland, Department of Applied Physics, 70210 Kuopio, Finland.
2Department of Applied Environmental Science, Stockholm University, SE-10691, Stockholm, Sweden.
3Department of Chemistry, Göteborg University, SE-41296, Göteborg, Sweden.
4Finnish Meteorological Institute, Helsinki, Finland.

Keywords: WARMING ARCTIC OCEAN, PRIMARY PARTICLES PRODUCTION, COMPOSITION, CLIMATE CONNECTION.

INTRODUCTION

The surface of open waters on Arctic Ocean has expanded during the last decades due to climate warming and consequent ice melting (Arrigo et al., 2008) and the sea ice extent has decreased critically especially during the last years, current autumn 2011 not being an exception. Climate models predict that a decline will continue in the future too but it is good to keep in mind that the previous predictions have so far mainly underestimated the autumn ice cover minima on the Arctic Ocean. The ice/snow melting Arctic has important effects on Arctic radiation budget and the climate due to the change in surfaces reflectivity and due to the possibility to produce new particles. For example, the ice melt areas of Arctic Ocean are able to produce radiatively active sized particles from sea water by bubble bursting. The composition and thus the properties of those particles could be dependent on e.g. the particle size, the water temperature and the biological activity of the water. However, the information is mainly missing at the moment. In this work, we concentrate on the composition of the lower end of Aitken mode bubble burst primary particles from clacier water, middle fjord water and open Arctic Ocean water.

METHODS

The Arctic Ocean bubble bursting laboratory experiments were carried out in a marine laboratory in Ny-Ålesund, on the island of Svalbald, located on a coast of the Arctic Ocean. The measurement period was between 20th August and 7th September 2009, being close to time of the ice extent minimum. The water samples were collected using a boat from three different point in order to see differences between different way effected waters: the clacier melting effected water were collected close to clacier in the end of Kongsfjorden with ice cubes around the sampling point, the fjord water were collected from the middle of Kongsjorden and the open Arctic Ocean water were collected on Greenland Sea close to the mouth of Kongsjorden.

The collected water was filled into a stainless steel tank situated in a laboratory. The water was pumped in a PET bottle where primary particles were produced by bubble bursting. The particle production was followed by measuring the particle size distribution. The water salinity, oxygen saturation and water temperature were measured too. An oxidized organic minimum volume fractions of the lower end of Aitken mode (15 nm – 60 nm) particles were studied as a function of particle size (15, 20, 30, 50 and 60 nm) using the UFO-TDMA (ultrafine organic tandem differential mobility analyzer; Vaattovaara et al.,
The analysis was carried out using the minimum organic volume fraction (OVF) analysis principle based on the measured growth factors (i.e. GF) introduced in Vaattovaara et al. (2006).

**RESULTS**

<table>
<thead>
<tr>
<th>Size/location</th>
<th>Middle fjord (+ 5 - 10 °C)</th>
<th>Greenland Sea (+ 5 - 10 °C)</th>
<th>Glacier water (+ 5 - 10 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OVF</td>
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<td>15 nm</td>
<td>51 %</td>
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<td>20 nm</td>
<td>47 %</td>
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<td>41 %</td>
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<tr>
<td>30 nm</td>
<td>38 %</td>
<td>39 %</td>
<td>37 %</td>
</tr>
<tr>
<td>50 nm</td>
<td>32 %</td>
<td>31 %</td>
<td>30 %</td>
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</tbody>
</table>

Table 1. The OVF for different sized bubble burst primary particles produced from Arctic Ocean water (salinity ca. 31-34 ‰) at Ny-Ålesund during polar summer.

**CONCLUSIONS**

The results show that the lower end of Aitken mode sized Arctic Ocean bubble burst particles include a remarkable amount of moderately oxidized material and the fraction change as a function of particle size. The smaller particles are, the higher the fractions are. The water sampling location did not make a big difference to the organic fractions of the particles. The composition change as a function of particle size should be further studied and consequently input to models.

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**REFERENCES**


AN EXPERIMENT FOR STUDYING THE EFFECT OF SOOT ON SNOW

A. VIRKKULA$^{1,2}$, O. JÄRVINEN$^2$, H. LIHAVAINEN$^1$, A. HYVÄRINEN$^1$, T. MÄKELÄ$^1$, N. KIVEKÄS$^1$, R. VÄÄNÄNEN$^2$, J. BACKMAN$^2$, A. HEIKKILÄ$^1$, A. AARVA$^1$, E.-M. KYRÖ$^2$, G. LEEUW$^{1,2}$

$^1$Finnish Meteorological Institute, P.O. Box 503, 00560 Helsinki, Finland
$^2$University of Helsinki, Department of Physics, P.O Box 64, 00014 Univ. of Helsinki, Finland

Keywords: soot, snow, albedo, irradiance

INTRODUCTION

Soot particles consists of light absorbing carbon, or black carbon (BC) and organics. If soot particles get deposited on snow they will absorb solar radiation, decrease the snowpack albedo and so heat the snow and accelerate its melting. This process has been studied for decades (e.g., Warren and Wiscombe, 1980; Clarke and Noone, 1985) and it is recognized as one of the most important climate forcers in the polar areas (e.g., Flanner et al., 2007; Quinn et al., 2008). Hansen and Nazarenko (2004) estimated that the soot effect on snow albedo may be responsible for as much as a quarter of the observed global warming. They further concluded that there is a need for more complete measurements of BC in Arctic snow and better quantification of the links to snow albedo, melting ice, and climate change (Hansen and Nazarenko, 2004).

The present project is aimed for studying the effects of soot on snow, for example the effect on albedo, snow grain size, and melting. Another interrelated aim is to study removal mechanisms: dry deposition and below-cloud snow scavenging of soot aerosols, since these are quantitatively not well known (e.g., Jylhä, 2000; Ying et al., 2004; Kyrö et al., 2009). The plan is to make experiments during several consequent winters. The first one of the series was conducted in spring 2011. Soot particles were produced and let them deposit on a snowpack on a farming field in southern Finland on Friday, 4 March 2011. Albedo and snowpack thickness were measured until all of it had melted. In addition, temperature profile, spectral radiation transmittance, and snow grain distribution within the snowpack were measured a month after the soot had been deposited on top of the snow, just before the most intensive melting started. In this work the first results are presented together with suggestions for following experiments.

METHODS

Soot was produced by burning organics in a wood-burning stove. The purpose was to get as high soot concentrations in air as possible, so that the effects become clear. The smoke was lead through a pipe, cooled by snow surrounding the pipe, and lead into a tent carage that was built on top of the snow. The other end of the tent carage was left open so that the smoke went out and a clear gradient was produced. An inlet was set at the open end of the carage tent and sample air was drawn to a measurement container approximately 5 meters apart. Aerosol number size distributions were measured with an SMPS, light scattering with a TSI 3360 nephelometer and absorption with a Radiance Research 3α PSAP. Outside the tent aerosol number concentrations were measured at several locations to get an estimate of the dispersion.

After the soot production was over, the tent carage was removed carefully from the area. Snow samples were taken from the deposit area and a background reference area, to be analyzed for organic and elemental carbon. The albedo of the snowpack was measured both over the deposit and the reference area. Snowpack thickness was measured by inserting 18 measurement sticks in a grid around the deposit area and the reference area, and inspecting them regularly. On 1 April, just when the fastest melting started,
two snow pits were dug, one in the deposit area and the other in the reference area. In both pits a physical characterization of snow stratigraphy was done, including thickness, density, hardness, grain size and shape. After that, temperature profiles were measured at a 5 cm intervals. In addition, the spectral irradiance at the depth of 20 cm was measured in the wavelength range 400 – 900 nm.

RESULTS AND DISCUSSION

Burning the organic material in the oven resulted in very high aerosol concentrations. The scattering coefficient ($\sigma_{SP}$) and absorption coefficient ($\sigma_{AP}$) were several thousands of Mm$^{-1}$ which is 2-3 orders of magnitude higher than in typical atmospheric conditions (Figure 1). Single-scattering albedo ($\omega_0$) was very low, approximately 0.2, showing that the burning really produced black carbon. Values below 0.2 are not realistic. They are probably due to uncertainties of both the nephelometer and the PSAP, and especially their different response times.

![Figure 1. Light absorption coefficient ($\sigma_{AP}$), scattering coefficient ($\sigma_{SP}$), and single-scattering albedo measured from the carage tent during the experiment.](image)

When the soot had been deposited on the snowpack the albedo of the dirty snow was clearly lower, $\sim 0.4 \pm 0.1$, than that of the reference area, $\sim 0.8$ for six days (Figure 2). On 10 March there was snowfall that can clearly be seen in the increase of the deposit area albedo to the same level as in the reference area. But the deposit area albedo soon decreased to lower values again. The reason is that the soot in the deposit area heats the snow around it and the fresh new snow melted away and exposed the soot deposits again. Another snowfall occurred on 19 March. This time both albedometers were covered by snow and there resulting data points were larger than one which is an artifact only. Just like after the previous snowfall, the deposit area albedo decreased faster than over the reference area. The last snowfall came on 28 March, and between 31 March and 6 April there was a steady decrease in both albedo and snowbed thickness. The decrease was approximately twice as fast in the deposit area as in the reference area (Figure 3).
As explained above, two snow pits were dug on 1 April, just before the fastest melting period started. The dirty snow was very clearly warmer than the clean snow (Figure 3). This shows that the soot within the dirty snow absorbed solar radiation and heated the surrounding snow, just as it was expected.
Figure 3. Vertical temperature profiles of the snowpack in the background area (clean) and in the soot deposit area (dirty), measured on 1 April. The vertical axis is the depth below the snow surface.

The spectral irradiances measured at the same time at 20 cm below the surface supports the interpretation that the higher temperature in the dirty snow was due to absorption of solar irradiation. In the wavelength range 400 to 700 nm the irradiances in the dirty snow were ~ 70 % lower than in the clean snow. In the near-infrared range 750 to 900 nm the irradiances were close to the same in both snowpacks but they were so close to the detection limits of the method that no conclusions can be drawn in this wavelength range.

Figure 4. Spectral irradiances at 20 cm below the snowpack surface of the background area (clean) and the soot deposit area (dirty), measured on 1 April.
CONCLUSIONS

The experiment demonstrated very clearly the effects of soot on snow: the albedo decreased, the snow grain size, the whole stratigraphy, and temperature profile changed compared with the reference site. All these lead to a faster melting of snow in the area where soot was deposited. The soot concentrations in the snow samples are still to be analyzed. It is expected that there will be a clear positive correlation between the soot concentration and melting rate. In this first experiment only two snowpits were dug. In the future experiments this will be done at several distances from the darkest snow so that it will be possible to interpolate the results to realistic ambient values – after all the general goal of the project is to reduce uncertainties related to the climate forcing by soot on snow.

The problem in the experiment was the very large variation in aerosol concentrations. This, on the other hand, was due to the method of soot production: organics were burned in a simple wood-burning stove. The use of this kind of a stove results in batch-like burning: refilling is not continuous, the stove is filled in after the previous batch has burned. Due to the high variability it was not possible to study any gradients in air, deposition velocities, and removal mechanisms, which is one of the objectives of this project. Therefore, in the following experiments soot will be produced by blowing cold soot particles without burning. This will make it possible to keep the concentrations in air at a quasi steady state and thus study also the removal mechanisms. A blower would have an other advantage as well: also other types of particles, for instance sand and volcanic dust could be blown on snow.

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AIRBORNE AEROSOL MEASUREMENTS IN SOUTHERN FINLAND

R. VÄÄNÄNEN, K. PAANANEN, S. SCHOBESBERGER, A. VIRKKULA, P.P. AALTO, T. POHJA, T. PETÄJÄ, M. KULMALA

1Division of Atmospheric Sciences, Department of Physics, University of Helsinki, Finland.

2Finnish Meteorological Institute, Helsinki, Finland

Keywords: aerosols, airborne, measurements, lower troposphere

INTRODUCTION

The role of the short-lived climate forcers (SLCF), such as natural and anthropogenic aerosols, ozone and methane, in the climate change is important, but still their exact net effect is poorly quantified (IPCC, 2007). To better understand the role of the aerosols in the lower troposphere airborne measurements are needed to support the long-term measurements at ground stations. Thus, Aerosol measurement group of University of Helsinki performs typically 2-3 airborne measurement campaigns each year starting in year 2009 to study the vertical profiles of ambient aerosols. The focus of these studies include the new particle formation events (S. Schobesberger et al, in prep.) and a prepared biomass burning experiment (A. Virkkula et al, in prep.). In this abstract we describe the measurements performed during a selected new particle formation event in October 2010.

METHODS

The airborne measurements of sub-micrometer aerosols were performed onboard a Cessna FR172F aircraft, which is equipped with aerosol measurement instrumentation. Air temperature and relative humidity were measured using a sensor mounted under the right wing of the aircraft. Static air pressure was measured inside the un-pressurized cabin. Isokinetic aerosol inlet was also mounted under the right wing. An inlet tube of around 3 m long brought the sample air to the aerosol and gas instruments, which were installed in a rack inside the cabin. These instruments included a ultrafine condensation particle counter TSI CPC 3776 with cut off size 3 nm (Mordas et al. 2008), a scanning mobility particle sizer (SMPS, Wang and Flagan,1998) with particle diameter range 10-320 nm, a CO2/H2O analyzer (LI-COR LI-840). A nephelometer (Radiance Research Model 903) and a triple wavelength (467, 530, and 660 nm) particle/Soot absorption photometer (PSAP, radiance research) were included in most of the campaigns. The flight track was recorded by a GPS receiver. A more detailed description of the instruments is in Schobesberger et al. (in prep).

The measurement flights were performed from and to Tampere-Pirkkala airport and the flight tracts were distributed over the area of Southern Finland. The flights were flown with a low airspeed (80 mph), and usually a measurement flight consisted of two steady climb-descent pairs to obtain vertical aerosol profiles. The maximum altitude reached with these flights was approximately 3.5 km.

RESULTS

On 13.10.2010 a new particle formation (NPF) event was observed at the SMEAR II station in Hyytiälä, starting from around 10 a.m., having the most intense growth phase between 10 a.m. and 15 p.m., whereas the growth of newly formed particles continued until 20 p.m. Two measurement flights were conducted during that day, partly concurrent with the NPF event. The first flight took place between 8 and 11 a.m., and it was thus flown at the same time as the first observations of fresh sub-5 nm particles at SMEAR II.
This flight followed a circular route south of Tampere and did not pass close to Hyytiälä. The latter flight of the day took place between 13 and 15 p.m., and passed the SMEAR II station at low altitude. Two climb-descent pairs were flown during both of the flights. We now concentrate to the profiles that are not flown near to Tampere to exclude the effects of anthropogenic sources. This means we analyze the second and third profiles of the both flights. This also enables us to compare the before-NPF situation to the situation where the particle growth is on-going. The wind direction during the flights was from North and the air masses arriving at the SMEAR II station originated from the Arctic Ocean. Previously this air mass trajectory has been identified as the most prominent for new particle formation events (Dal Maso et al. 2005, Sogacheva et al. 2008).

Figure 1A shows the ground-based particle size distribution as observed by the SMEAR II station on that day. The lower panel depicts total particle number concentrations, and the times when the studied profiles were flown are marked with different colors. The upper row in Figure 1B presents the particle number size distributions from the airborne measurements using the SMPS and the stand-alone CPC for each of the four profiles (first four columns from the right), as well as the total number concentrations as measured by the CPC (fifth column). In the particle number size distributions, the range from 10 to 320 nm is obtained directly from the SMPS whereas the lowest size bin, with a nominal mean particle size of 5 nm, is calculated using the difference of the total concentration as measured by the CPC (cut-off size of 3 nm) and the integrated concentration from the SMPS. This means that we assume that the amount of particles with the diameter larger than 320 nm is insignificant. The altitude axis is divided into bins of 100 m, and the average distributions are calculated for each altitude-bin. The lower row of panels compares the size distributions obtained from ground-based measurements to the airborne measurements at the lowest altitude bin of each profile.

When comparing the airborne particle size distributions at the lowest altitudes to the size distributions measured at the SMEAR II station in Hyytiälä, one can see that the airborne measurements reproduce relatively well the shapes of the particle distributions measured at the same time at SMEAR II. This holds when the low altitude measurements are done spatially 100-200 m from the SMEAR II station, which is the case for the third and fourth profile, but also when the spatial distance between the measurements is more than 120 km, which is the case for the first and second profiles. The regional area with uniform aerosol airmass can thus be several hundred kilometers wide (O’Dowd et al. 2009). This corroborates the initial assumption that the regionality of the NPF events. As the formation and subsequent growth is detected in a fixed measurement station, this process needs to occur in a homogenous air mass (Dal Maso et al. 2007).

The vertical total concentration profiles are plotted in the right-upper-most panel of Figure 1B. The profiles measured before the NPF burst began (1-2) have lower concentrations inside the boundary layer than the profiles measured afternoon (3-4) when the particle formation and growth is on-going. Also, when comparing the total concentrations inside the boundary layer of third and fourth profile, the concentrations increased between these flights. Also, the top of the boundary layer height developed from 1000 m up to 1300-1400 m between the flights.

CONCLUSION

Airborne aerosol particle size distribution was measured in the lower troposphere over the area of Southern Finland during a new particle formation event. The measurements were performed using a small Cessna 172 aircraft, and the particle size distribution was measured using an ultrafine condensation particle counter TSI 3776 and a scanning mobility particle sizer. We observed a regional new particle formation event with a wide at least 120 km, and we observed the new particle formation happen through the boundary layer.
Figure 1. A: Particle number size distribution and the total number concentration as measured by the DMPS at the SMEAR II station in Hyytiälä on the 13.10.2010. The airborne measurements were performed during the time between the dotted lines. B: The four left top panels show particle size distribution as measured by the stand-alone CPC and the SMPS onboard the aircraft during the four vertical profiles. The right-most top panel shows the total number concentrations during the profiles, measured by the stand-alone CPC. The second row presents the particle number size distributions of the lowest measured altitude in comparison to the average particle size distribution at Hyytiälä.
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SEASONAL VARIATIONS IN CARBON DIOXIDE EMISSIONS FROM LAKES AND STREAMS

GESA A. WEYHENMEYER1,2, PIRKKO KORTELAINEN3, SEBASTIAN SOBEK1, ROGER MÜLLER1 and MIITTA RANTAKARI1,4

1 Department of Ecology and Genetics/Limnology, Uppsala University, Norbyvägen 18D, 752 36 Uppsala, Sweden
2 Department of Aquatic Sciences and Assessment, Swedish University of Agriculture, Box 7050, 750 07 Uppsala, Sweden
3 Finnish Environment Institute, Box 140, FI-00251 Helsinki, Finland
4 Finnish Forest Research Institute, Box 18, FI-01301 Vantaa, Finland

Keywords: carbon, CO₂, climate, seasonality, boreal, lake, stream

INTRODUCTION

Despite the small fraction of the surface of the Earth occupied by streams, rivers, ponds, lakes and reservoirs a variety of studies show that inland waters play an important role in the global carbon cycle [Aufdenkampe et al., 2011; Battin et al., 2009; Cole et al., 2007; Kosten et al., 2010; Richey et al., 2002; Tranvik et al., 2009]. The studies clearly demonstrate that inland waters are highly active sites for transport, transformation and storage of considerable amounts of carbon received from the terrestrial environment [Tranvik et al., 2009] has for example shown that the annual loss of 2 Gt is similar to the annual total global net ecosystem production. Such global estimates include, however, large uncertainties. One large uncertainty concerns seasonal and daily variations of carbon dioxide (CO₂) fluxes from inland waters. So far, global estimates are based upon day-time CO₂ emissions from inland waters with a clear bias towards summer values in the Northern Hemisphere north of 40°N [Cole et al., 2007; Tranvik et al., 2009]. Day-time summer CO₂ values might overestimate CO₂ emissions of heterotrophic systems, typical for the large boreal region [Cole et al., 1994], since photo- and microbial carbon transformations, known to drive CO₂ emissions in heterotrophic systems [Kaiser and Sulzberger, 2004; McCallister et al., 2005] have been shown to be enhanced by increased sunlight and increased water temperatures [Bergström et al., 2010; Gudasz et al., 2010; Vähätalo et al., 2003], typically occurring during summer at day-time. Thus, CO₂ emissions from inland waters, here expressed as CO₂ partial pressure (pCO₂), might increase towards summer and decline again thereafter provided that increasing efficiency in photosynthesis does not counteract the increasing efficiency in photo- and microbial transformation in heterotrophic systems towards summer. Such increases in CO₂ emissions towards summer have, for example, been observed in a lake in Northern Sweden [Jonsson et al., 2007]. CO₂ emissions from inland waters might, however, also decrease towards summer along with decreasing hydrological inputs of CO₂ and dissolved organic carbon (DOC) from terrestrial ecosystems that have been found to be important drivers for pCO₂ variations in surface waters [Humborg et al., 2009; Stets et al., 2009; Striegl and Michmerhuizen, 1998]. The influence of hydrological inputs of CO₂ and DOC on pCO₂ in lakes is supported by a variety of studies showing that precipitation is one of the best predictors for CO₂ concentrations both in boreal and tropical lakes [Marotta et al., 2010; Rantakari and Kortelainen, 2005]. Decreasing pCO₂ towards summer has also been observed by e.g. [Atilla et al., 2011; Kelly et al., 2001; Kortelainen et al., 2006]. In addition to hydrological controls [Kelly et al., 2001] attributed the summer pCO₂ decline to the influence of thermal stratification which reduces the ratio epilimnetic area to the epilimnetic volume (Ae/Ve). Considering that epilimnetic sediments are an important site of degradation of organic carbon to CO₂, they suggested that a reduction in Ae/Ve resulted in a dilution of CO₂ in the epilimnion and thus in a pCO₂ decline towards summer. A stratification effect on pCO₂ has also been observed by [Åberg et al., 2010]. They found that as soon as the epilimnion deepened, pCO₂ in the surface water of a relatively small (3.8 km²) and deep (mean depth: 5 m, maximum depth 17 m) lake increased as a consequence of
METHODS, RESULTS and DISCUSSION

To evaluate spatial and temporal \( pCO_2 \) variations in lakes and streams we used water chemical data from more than 700 boreal lakes and more than 60 boreal streams distributed over Sweden and Finland. Our data material showed large spatial and temporal variations where \( pCO_2 \) in lakes and streams reached minimum values during summer. In streams we expect \( pCO_2 \) primarily be driven by hydrological conditions. Accordingly, we found highest water discharges and highest \( pCO_2 \) values during spring and lowest ones during summer. \( pCO_2 \) in streams co-varied best with \( NO_3-N \) concentrations, probably because of a close interactions between \( NO_3-N \) consumption and \( CO_2 \) production in nitrogen limited terrestrial ecosystems. Hydrological conditions and catchment processes probably counteracted the influence of photo- and microbial transformations which we expected to result in increased \( pCO_2 \) during summer. An antagonistic effect of water discharge and photo- and microbial transformation on \( pCO_2 \) during summer might give an explanation why water discharge decreased faster towards summer than \( pCO_2 \) in streams.

Hydrological conditions and catchment processes are likely to have an important impact not only on \( pCO_2 \) in streams but also on \( pCO_2 \) in small and shallow boreal lake waters, here indicated by high \( pCO_2 \) values in lake waters at high water discharges in spring and low \( pCO_2 \) values at low water discharges in summer. During summer, however, streams and lake waters function differently, causing our observed significantly lower \( pCO_2 \) values in surface waters of lakes than in streams. Most obvious differences between lakes and streams during summer are influences of thermal stratification and photosynthesis. Photosynthesis is expected to result in decreasing \( pCO_2 \) during day-time. We did not have data on photosynthesis in our lakes but based on measurements on boreal lakes in general (e.g. [Einola et al., 2011]) we assume that photosynthesis is only a minor process influencing \( pCO_2 \) in our heterotrophic boreal lakes. Thermal stratification, however, was pronounced, albeit our lakes were rather small and shallow. The influence of thermal stratification on biogeochemical cycling in lakes is well known [Keller, 2007]. Thermal stratification can result in nutrient depletion in the epilimnion and oxygen depletion in the hypolimnion as element exchanges between epi- and hypolimnion are hindered by a thermocline. Assuming that large parts of \( CO_2 \) are produced at the sediment-water interface or enter the hypolimnion via groundwater a strong thermocline will result in \( CO_2 \) accumulation in the hypolimnion. The \( CO_2 \) accumulation in the hypolimnion occurs at the same time as \( O_2 \) is consumed. Consequently, \( O_2 \) concentrations have earlier been shown to be well related to \( CO_2 \) concentrations. In 177 randomly selected Finnish lakes, for example, as much as 79 % of the variation in \( CO_2 \) could be explained by \( O_2 \) concentration only [Kortelainen et al., 2006]. Since we also found a clear relationship between \( O_2 \) concentrations and bottom water \( pCO_2 \) we suggest that thermal stratification plays a decisive role for \( pCO_2 \) seasonal variation in lakes in addition to hydrological processes that in our case co-varied with the intensity of thermal stratification. We observed strongest thermal stratification and one of the lowest water discharges in July. Accordingly \( pCO_2 \) in lake surface waters reached its minimum in July. A strong relationship between intensity of thermal stratification and \( pCO_2 \) in the epilimnion was found both in Swedish and Finnish lakes but Finnish lakes had constantly lower \( pCO_2 \). We suggest that the lower \( pCO_2 \) in the Finnish lakes are a result of higher pH values, probably caused by larger lake volumes giving a better buffering capacity and by a higher relative importance of agriculture in the catchment area [Rantakari and Kortelainen, 2005]. Thus not only the strength of thermal stratification, strongly determined by lake depth, but also other lake morphometric variables such as the water volume have an influence on \( pCO_2 \) which has also been reported by [Sobek et al., 2003]. In general lake morphometry determines the relative importance of processes driving \( pCO_2 \) which in some cases might cause deviating results between lake ecosystems.

Once thermal stratification is over and water column mixing starts, \( pCO_2 \) becomes similar between lakes and streams provided that pH values are in the same range. During mixing surface water \( pCO_2 \) reaches maximum values during the open water period. These results correspond to the findings of [Bellido et al., 2009; Huotari et al., 2009; Laurion et al., 2010] who all found maximum gas losses
during mixing periods, although highest surface water concentrations have been reported during the winter ice cover period [Kortelainen et al., 2006]. However, despite water mixing we observed \( p_{\text{CO}_2} \) in bottom waters being higher than in surface waters. We also observed \( p_{\text{CO}_2} \) in bottom waters being higher than stream waters during all seasons. These results indicate that the residence time of \( \text{CO}_2 \) is much higher in lakes than in streams and they might even indicate a higher \( \text{CO}_2 \) production in lakes than in streams.

Although \( \text{CO}_2 \) might primarily be produced already in the catchment or at the sediment-water interface we have indications for epilimnetic \( \text{CO}_2 \) production since we found decreasing AbsF_{420}/DOC ratios in surface water of lakes towards summer. Decreasing AbsF_{420}/DOC ratios correspond to a preferential degradation of coloured organic matter which has been observed for waters that have been exposed to solar radiation, suggesting a strong influence of photomineralization ([Moran et al., 2000; Vähätalo et al., 2000]. Seasonal variations in AbsF_{420}/DOC were not detectable for streams, probably because of other processes overriding the effect of photomineralization in typically shaded boreal streams.

CONCLUSION

From our results we conclude that seasonal \( p_{\text{CO}_2} \) variations in boreal lakes follow water discharge and thermal stratification patterns. Thermal stratification causes high seasonal \( p_{\text{CO}_2} \) variations with minimum \( p_{\text{CO}_2} \) values during summer in the epilimnion (Fig. 1). If such minimum \( p_{\text{CO}_2} \) values are the basis for annual flux estimates on a global scale, \( \text{CO}_2 \) fluxes from inland waters into the atmosphere will probably slightly be underestimated. More research on seasonal and also on daily \( p_{\text{CO}_2} \) variations is needed to decrease uncertainties in global estimates.

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INFLUENCE OF WATER TEMPERATURE, SALINITY AND OXYGEN SATURATION ON SEA SPRAY AEROSOL EMISSIONS FROM ARCTIC OCEAN WATER

J. ZÁBORI1, R. KREJCI1, A.M.L. EKMAN2, E.M. MÅRTENSSON1,2, E.D. NILSSON1,
F.R. ALEXANDER1, J.O. NATHAN2 and D.H. CHAPMAN2

1Department of Applied Environmental Science, Stockholm University, Stockholm, SE-11418, Sweden
2Department of Meteorology, Stockholm University, Stockholm, SE-10691, Sweden
3Department of Earth Sciences, Uppsala University, SE-752 36 Uppsala, Sweden

Keywords: marine aerosol emissions, Arctic Ocean, Svalbard

INTRODUCTION

Sea ice extent in the Arctic region has continuously declined over the last decades, presumably as a result of global warming. As a consequence, the source area of primary marine aerosol is growing, which likely increases the marine primary aerosol emissions in the Arctic (Nilsson et al., 2001). Sea ice melt and larger areas of ice-free ocean will also influence the general circulation in the Arctic and as a consequence alter the wind speed pattern over the ocean. Wind speed is a main driving force of marine primary aerosol emissions. The magnitude of these changes is still not clear. Besides wind speed, also other parameters, such as water temperature and salinity influence the intensity of primary marine aerosol emissions. In contrast to the wind speed effect, the influence of these can be easily studied with in laboratory controlled conditions. In laboratory experiments with artificial sea water it has been shown that aerosol particle number emissions and size distributions change with water temperature and salinity (Mårtensson et al., 2003) and dissolved oxygen. This study examines links among water temperature, salinity, oxygen saturation changes and intensity of primary marine aerosol emissions from Arctic Ocean waters.

METHODS

Two measurement campaigns were carried out in the Marine Laboratory at Ny-Ålesund, Svalbard (78° 55´ N, 11° 56´ E) as a part of the interdisciplinary climate project GRACE (The Green House Arctic Ocean and Climate Effects of Aerosols). The first one was conducted during the Arctic late summer (20th August 2009 – 7th September 2009). The second one took place from 12th February – 8th March 2010. Surface sea water was sampled from different locations by a small boat during the summer campaign. The sampling locations were situated close to the glacier front, in the middle of the Kongsfjorden and outside the fjord representing conditions of the open sea. During winter, when the use of the boat was not possible, open sea surface waters were collected from shore along the coast line at the north-west side of the Broggerhalvoya peninsula. Waters possibly influenced by melting glaciers were sampled by boat close to the glacier front in Kongsfjorden. In addition, experiments with deep fjord sea water from 80 m depth available directly at the marine laboratory were conducted during both measurement campaigns. The collected water sample was filled into a stainless steel tank situated in the marine laboratory. From there it was pumped into a PET bottle where aerosols were produced through bubble bursting, generated by artificial water flow. Aerosol number concentrations were measured for the particles with a dry diameter of 0.01 µm to 5 µm by a Condensation Particle Counter (CPC) and for diameters from 0.25 µm to 32 µm by an Optical Particle Counter (OPC). Salinity, water temperature and oxygen saturation were measured continuously during the experiments. Detailed description of the methodology can be found in (Hultin et al, 2010).
RESULTS

The strongest relation between environmental conditions and the intensity of primary marine aerosol emissions was found for the water temperature (Figure 1).

![Figure 1: Relationship between water temperature and particle number concentration for sea water sampled at the open sea outside the fjord. Blue indicates results of the winter campaign, whereas red displays the results of the summer campaign. Although displayed are median values for particle number concentration and water temperature and 25th and 75th percentiles (dashed lines).](image1)

Higher total particle number concentrations were observed consistently for lower water temperatures, both for particles measured by the CPC and the OPC. The relation between sea water temperature and sea spray aerosol emissions intensity is not linear and shows instead more exponential decrease with increasing temperature. For water temperature higher than 7 °C there is nearly no trend observed. An extension of the analysis by including also the salinity is presented in Figure 2. In this case all different types of sampled waters are considered, including samples collected inside the fjord and near the glacier.

![Figure 2: Median water temperatures and salinities for different particle number concentrations.](image2)

A clear water temperature effect on the particle number concentration is still visible, whereas a clear relation between sea water salinity and sea spray emission intensity is missing. A similar conclusion was observed in the case of the relationship between oxygen saturation, water temperature and particle number concentration (Figure 3).
Figure 3: Median water temperatures and oxygen saturations for different particle number concentrations.

CONCLUSIONS

The first results from laboratory experiments studying primary marine aerosol emissions from Arctic Ocean waters show that sea water temperature is the most important sea water parameter influencing primary marine aerosol emissions. The exponential trend of decreasing sea spray emission intensity with increasing water temperature has potentially large implications for future evolution of aerosol sources importance and consequently cloud properties and aerosols related climate radiative forcing in the Arctic. Diminishing sea ice will result in decreased surface albedo and in a form of positive feedback contribute to the warming of the Arctic. On the other hand, larger areas of open sea will provide a stronger source of sea spray aerosol, which in turn can act in form of a negative feedback by increasing aerosol scattering (direct radiative forcing) and by modifying cloud microphysical properties providing additional cloud condensation nuclei (aerosol indirect effect). However, the complete picture is more complex and additional effects, such as increased water vapour concentration and changing general circulation patterns for example have to be taken into account.

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EVAPORATION RATES OF LEVOGLUCOSAN SUBMICRON PARTICLES

N. ZANNONI¹, T. ROSENOERN¹, A. A. ZARDINI² and M. BILDE¹

¹ Dept. of Chemistry, University of Copenhagen, 2100 Copenhagen Ø, Denmark.
² European Commission- Joint Research Centre, Institute for Energy, Sustainable Transport Unit, Ispra, Italy.

Keywords: Levoglucosan, saturation vapour pressure, enthalpy of vaporization.

INTRODUCTION

Aerosol particles influence climate, air quality and human health¹². To quantify these effects it is important to have knowledge on the composition, the physico-chemical properties, and phase partitioning of particles components. This information is especially demanded for the components of the organic fraction, which is very complex and highly variable in space and time³. For this reason the volatility of levoglucosan particles was the object of this study. Levoglucosan is an anhydro sugar primarily emitted from the combustion of biomass, and being the most abundant product from the decomposition of cellulose it is considered a good tracer compound for biomass burning⁴⁵. It has been detected in large concentrations in urban, forest, remote sites⁶⁷, and in Arctic ambient air⁸. The volatility of levoglucosan was investigated through a modified Tandem Differential Mobility Analyzer (TDMA) set up coupled to a laminar flow tube. A value of the saturation vapour pressure of levoglucosan was then inferred by using mass transfer theory⁹¹⁰. Finally, the evaporation rates were studied in the temperature range of 15°C- 35°C in order to calculate the enthalpy of transition of levoglucosan. We here present the first preliminary results of this study.

METHODS

A modified TDMA combined with a laminar flow reactor was used to measure the evaporation rates of single component levoglucosan particles in the initial size range of 50-100 nm. A ~10⁻⁴ mol/L aqueous solution of levoglucosan was prepared and then atomized to obtain a polydisperse aerosol. This was first dried and then charged to a known charge distribution. A Differential Mobility Analyzer was used to select a narrow size range of the polydisperse aerosol. The selected particles entered a 3.5 meters long flow tube, where a sheath flow was employed in order to keep the aerosol flow laminar. Finally, a Scanning Mobility Particle Sizer composed of a second DMA coupled to a Condensation Particle Counter was used to measure the size distribution and aerosol concentration along the experimental set up. The difference in sizes measured along the flow tube as a function of the residence time gave the evaporation rate of the investigated system. The aerosol and sheath air flows were calibrated with a Gillibrator flow meter, each time a new experiment started. The aerosol flow was calibrated to 0.3 L/min, while the sheath air inside the flow tube was 0.6 L/min, for all the experiments. The size distributions were collected at seven different sites along the set up: at the DMA, before entering the reactor, at four different ports inside the reactor, and at the end of it. In some experiments, the measurements were run just at the initial and final port of the flow tube. The measurements were conducted at 15°C, 21.5°C, 25°C, 30°C, and 35°C temperature, and at RH~2%. A lognormal function was fitted to the measured size distributions and then employed in the calculation of the vapour pressure. In addition, by relating the vapour pressure to the experimental temperature it was possible to find a value for the enthalpy of transition of this compound (Eq.1).
\[ \log P^o = -\frac{\Delta H_{\text{trans}}}{2.303 \cdot R \cdot T} + C \] (1)

RESULTS

Figure 1. Evaporation rates of levoglucosan particles at 35°C. Particles of initial diameter of 200, 150, 100, 90, 80, 70, 60, 50 nm were tested in this experiment.

Figure 2. Temperature dependent evaporation rates of 100 nm levoglucosan particles at 15°C (blue), 21.5°C (black), 25°C (red), 30°C (green) and 35°C (pink). The data points correspond to fitted values of the size distributions measured at different sites along the experimental set up. Lines were added to help to guide the eye.
CONCLUSION

Based on supplementary experiments and literature research to be presented at the meeting, we believe that the particles exist in the metastable liquid phase. While further experiments and data analysis is still on-going, a preliminary value of the sub-cooled vapour pressure of levoglucosan inferred from measurements of evaporation rates of sub-micron particles at RH~2% and 21.5°C is \( \sim 5 \times 10^{-5} \) Pa.

The obtained enthalpy of vaporization for the temperature range of 15°C-35°C was found to be 97.6±10.56 KJ/mol.

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SOSAA – A BOUNDARY LAYER MODEL FOR LONG TERM STUDY OF PARTICLE FORMATION AND GROWTH WITH DETAILED CHEMISTRY AND AEROSOL DYNAMICS

L.ZHOU1, M.BOY3, H.VUOLLEKOSKI1, C.WATCHARAPASKORN1, D.MOGENSEN1,
S.SMOLANDER1, A.SOGACHEV2 and M.KULMALA1

1Department of Physics, University of Helsinki, Finland.
2Wind Energy Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Denmark.

Keywords: BOUNDARY LAYER MODELLING, PARTICLE FORMATION AND GROWTH, AEROSOL DYNAMICS.

INTRODUCTION

Natural and anthropogenic aerosols may have a great impact on climate as they can directly interact with solar radiation and indirectly affect the Earth’s radiation balance and precipitation by modifying clouds. In order to quantify the direct and indirect effects, we must understand the complex processes that connect an aerosol particle to a cloud droplet. However, while modern measurement techniques are able to detect particle sizes down to nanometre all the way from ground up to the stratosphere, the data do not serve for all of our needs for understanding the processes. Hence we will demonstrate a modelling approach to investigate the complex processes of aerosols in the atmospheric boundary layer (ABL).

METHODS

SOSAA (model to Simulate the concentration of Organic vapours, Sulphuric Acid, and Aerosol) is the first column model existing in the world with detailed chemistry and aerosol dynamics parallelized. It can be used to study aerosol processes in the ABL for long period. The model includes the aerosol dynamics module UHMAEMO (University of Helsinki Multicomponent Aerosol Module) coupled with the chemistry-transport column model SOSA (model to Simulate the concentration of Organic vapours, Sulphuric Acid, Figure 1).

Figure 1. SOSAA model structure
SOSA attempts to reconstruct the emissions, transport, and chemistry in the ABL in and above a vegetation canopy using meteorological measurements (Boy et al., 2011). UHMAEMO simulates tropospheric new particle formation in clear sky conditions. It is developed from the UHMA model which includes all basic aerosol dynamical processes: nucleation, condensation, coagulation and dry deposition (Korhonen et al., 2004).

CONCLUSIONS

As a first application of the model, we present nucleation studies for the year 2010 in Hyytiälä, Finland with different nucleation theories including homogeneous nucleation of sulphuric acid and water, kinetic nucleation, and activation nucleation. Modelled particle growth rates and sulphuric acid concentrations have also been compared with measurements from HUMPPA-COPEC campaign, which was carried in Hyytiälä from 5th July to 13th August, 2010.

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