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INTRODUCTION

The Centre of Excellence in Atmospheric Science – from molecular and biological processes to the global climate (CoE ATM) has its fourth year ongoing. In this paper we give an overview on the development of our research activities and summarize the main scientific achievements of the past year.
Earth’s system is facing several environmental challenges on a global scale, so-called “Grand Challenges”. The growing population needs more fresh water, food and energy, which will cause challenges such as climate change, declining air quality, ocean acidification, loss of biodiversity and shortages of fresh water and food supplies. Grand Challenges are the main factors controlling human well-being and the security and stability of future societies. Since the Grand Challenges are highly connected and interlinked, they cannot be solved separately. Therefore, a framework is needed in which a multidisciplinary scientific approach has the required critical mass and is strongly connected to fast-tracked policy making. The potential solutions are typically tightly coupled with each other.

According to the latest assessment by intergovernmental Panel for Climate in 2014, scientists are more than 95% certain that major part of the global warming is caused by increasing concentrations of greenhouse gases and other human (anthropogenic) activities. Climate change research aims to better understand past and predict future climate by using observations and theoretical models. Results from atmospheric research can also be directly applied to human health; in Finland the small particles in the atmosphere shorten the average life time expectancy by few months, but e.g. in China the effect is several years. Changes in climate and air quality depend on both natural and man-made emissions, as well as various physical, chemical and biological processes occurring in the atmosphere, biosphere and at their interface. To monitor, model and seek solutions for these grand challenges needs a systemic approach with both scientific excellence and strong cooperation with the various interest and stakeholder groups. This requires contributions from a new type of science that links disciplines, knowledge systems and societal partners to support a more agile innovation system.

The core of the ATM research activities is the COBACC (COntinental Biosphere-Aerosol-Cloud-Climate) feedback. Atmosphere is in close interaction with the biosphere, hydrosphere, cryosphere and lithosphere on time scales from seconds to millennia (Wanner et al., 2008). Kulmala et al. (2004) hypothesised that higher temperatures and CO$_2$-levels boost continental biomass production, leading to increased biogenic secondary organic aerosol (BSOA) and cloud condensation nuclei (CCN) concentrations, tending to cause cooling. The COBACC feedback has two major overlapping feedback loops, both initiated by increased CO$_2$ concentrations (Kulmala et al., 2013, 2014). In addition to affecting CCN, BSOA changes condensation sink, total aerosol surface area and volume in the atmosphere, which changes the ratio of diffuse to total sun radiation, which has feedback to gross primary production (GPP). The focal points of these two loops are thus ambient temperature and GPP. The feedback loops combine physical, chemical and biotic phenomena. The COBACC feedback can be considered as a broad framework, which connects the human activities, the continental biosphere, and the changing climate conditions.

In the current CoE ATM, we have expanded our approach in two complementary ways: i) by considering a full set of feedback loops associated with COBACC including all the relevant processes and biogeochemical cycles, and ii) by covering all the major continental regions. This is possible with a help of continuous and comprehensive in situ observations in various environments and ecosystems, ground- and satellite-based remote sensing, targeted laboratory experiments, multi-scale modelling, and earth observation techniques.

**AIMS**

Feedback mechanisms are essential components of our climate system, as they either accelerate or slow down changes in climate-related quantities in the presence of external forcings. Prior to the ongoing CoE funding, we had qualitatively solved the terrestrial climate feedback loop connecting the increasing atmospheric carbon dioxide concentration, changes in gross primary production (GPP) associated with the carbon uptake, organic aerosol formation in the atmosphere, and transfer of both diffuse and global radiation. During the ongoing CoE funding period 2014-2016, we have now provided the first quantitative estimate regarding this feedback combining process-level understanding with comprehensive, long-term
field measurement data set collected from a boreal forest site SMEAR II (Kulmala et al. 2014b, Fig. 1). Our estimate of the gain in GPP resulting from the feedback is larger than the gains of the few atmospheric chemistry-climate feedbacks estimated using large-scale models (Kulmala et al. 2014b). Our analysis demonstrates the power of using comprehensive field measurements in investigating the complicated couplings between the biosphere and atmosphere on one hand, and the need for complementary approaches relying on the combination of field data, satellite observations model simulations on the other hand.

The main scientific objective of ATM is to quantify the COBACC feedbacks in changing climate. In order to do this, we will:

(i) find out and quantify the main climatic feedbacks and forcing mechanisms related to aerosols, clouds, precipitation, biosphere-atmosphere and cryosphere-atmosphere interactions,
(ii) develop, refine and utilize the newest measurement techniques and modeling tools scaling from quantum chemistry to global Earth System Observations and Models,
(iii) create a deep and quantitative understanding on the role of atmospheric clusters and aerosol particles in local and global biogeochemical cycles of water, carbon, sulfur and nitrogen and their linkages to the atmospheric chemistry, and
(iv) integrate the results in the context of regional and global scale Earth system understanding.

During the coming CoE funding period 2017-2019, our objective is to quantify the COBACC feedback mechanisms and expand the understanding to cover various environments. The ultimate aim is to produce a quantitative estimate of the climate feedback loop first for boreal and arctic climate regions and finally for the global climate. The specific objectives that have been updated/added are:

1. To find out and quantify the main climatic feedbacks and forcing mechanisms related to aerosols, clouds, precipitation, biosphere-atmosphere and cryosphere-atmosphere interactions by:
   • Extension of the comprehensive, continuous and long-term observations of atmospheric composition (aerosols, ions, trace gases, clusters, greenhouse gases) to other arctic and boreal environments and to targeted field studies globally
   • Capacity building of atmospheric composition measurement and data interpretation in selected, currently underrepresented areas, such as Russia and China
   • Analyzing the potential impacts of climate change on ecosystem processes e.g. by experimenting in forested ecosystems using the highly instrumented world-class observatories
   • Unraveling the effects of disturbance mechanisms such as extreme weather events and wild fires on processes underlying GHG and BVOC fluxes between ecosystems and the atmosphere in boreal and arctic areas, including permafrost regions

2. To develop, refine and utilize the newest measurement techniques and modeling tools scaling from quantum chemistry to global Earth System Observations and Models by:
   • Chemical sensors further developed for monitoring of amines
   • Increased attention to primary biological aerosol particles from different ecosystems
   • Versatile and flexible solid phase microextraction based air sampling systems, further developed for in-situ analysis of different chemical compounds
   • Expansion of the ground-based observations to the atmospheric column with ground-based and satellite borne remote sensing and aircraft observations and integrating data analysis including new optical products such as SIF and PRI
• Expansion and utilization of the unique time series on metabolic processes controlling the biogeochemical cycles in ecosystems
• Improved observation capacity for OH reactivity, trace gases, atmospheric ions and clusters, radicals, atmospheric aerosols, and clouds

3. To create a deep and quantitative understanding on the role of atmospheric clusters and aerosol particles in local and global biogeochemical cycles of water, carbon, sulfur and nitrogen and their linkages to the atmospheric chemistry by:
• Clarifying the amine reactions in the atmosphere and the effects on aerosol particle formation under atmospheric conditions by different chemical measurements
• Clarifying and quantifying contribution of ELVOCs on new particle formation and formation of secondary organic aerosols
• Defining the most important physical and chemical factors controlling the cloud droplet activation of atmospheric aerosols and developing a simplified thermodynamic presentation to describe the activation

4. To integrate the results in the context of regional and global scale Earth system understanding by participating in international research initiatives:
• CoE ATM has joined the European consortium of EC-Earth. The EC-Earth model is developed by over 20 institutes around Europe, and ATM CoE will pursue a significant role in the core development team. EC-Earth will provide a state-of-the-art global numerical laboratory for studying the main scientific questions of ATM CoE. ATM CoE will develop necessary processes in EC-Earth, including BVOC emissions, SOA formation and aerosol-cloud interactions. Furthermore, EC-Earth will be applied to quantify the COBACC feedback loops.
• CoE ATM is participating Coupled Model Intercomparison Project phase 6 (CMIP6) with EC-Earth, both in terms of developing the CMIP6-version and providing CMIP6 simulations for the consortium. EC-Earth development at CoE ATM will ensure that the core processes and interactions of COBACC are adequately incorporated. The close integration to the CMIP6 process provides a link to following IPCC reports.

METHODS

The ATM scientific approach is to combine i) continuous and comprehensive in situ observations in different types of environments or ecosystems and platforms, ii) ground- and satellite-based remote sensing, iii) targeted laboratory experiments and iv) multi-scale modeling efforts, in order to provide improved conceptual understanding over the relevant spatial and temporal scales. With this approach we are able to improve fundamental process understanding and to clarify the implications of the processes over the relevant spatial and temporal scales.

We have divided the work into four work packages which cover the relevant temporal and spatial scales. The work packages form a continuum from nano and micro scales to regional and further to global scale. The comprehensive observations and hierarchical modeling tools together with open data archives used in an integrative manner in combination with global GHG, aerosol and ecosystem networks enable us to study the different cycles and feedbacks.

INFRASTRUCTURE AND DATA MANAGEMENT

CoE ATM research infrastructure (INAR RI) belongs to the Finnish RI roadmap 2014-2020. With its research infrastructure and networks, CoE ATM acts as the backbone of the research in atmospheric sciences and atmosphere-biosphere interactions in Finland. CoE ATM is the national focal point of Finnish activities in four European research infrastructures: ICOS (Integrated Carbon Observation System), ACTRIS (Aerosols, Clouds, and Trace gases Research Infrastructure), eLTER (European Long-term Ecosystem Research) and AnaEE (Infrastructure for Analysis and Experimentation on Ecosystems).
The research unit operates five field stations in Finland: the four SMEAR (Station for Measuring Forest Ecosystem Atmosphere Relations) stations and GAW (Global Atmosphere Watch) station in Pallas-Sodankylä. The SMEAR II is the world leading station on ecosystem-atmosphere data due to its comprehensive research program and its unique time series of aerosol formation and biogeochemical fluxes. CoE ATM is also intensively involved in developing Global SMEAR network. SMEAR stations have already been established in China (Nanjing) and Estonia (Järve). Establishment of global network of ecosystem-atmosphere stations is also one core aim in the Pan-Eurasian Experiment (PEEX) that has now taken the first steps towards implementing its science plan.

Research laboratories include Aerosol Laboratories in the Universities of Helsinki and Eastern Finland and in Finnish Meteorological Institute, Ecophysiological laboratory and Laboratory for Analytical Chemistry in the University of Helsinki. Research is also done in CERN Cloud Chamber, Leibniz-Institute for Tropospheric Research Laminar Flow Tube and Plant and reaction chamber facility at Forschungszentrum Jülich, Germany. In addition to ongoing field monitoring, field campaigns and laboratory data, we use large scale remote sensing data of climate, and modelling at different spatial and temporal scales.

CoE ATM’s data policy follows the general guidelines of “Science Europe Principles on Open Access to Research Publications”. Raw measurement data and other documentation collected at the measuring stations are copied hourly or daily to the dedicated processing server of UH. The original data are also kept at the stations. The online-processed data are inserted automatically into SMEAR database (hosted by CSC). Manual processing and check of data is done by the responsible researchers. The final end-user data are periodically arranged into yearly datasets that are archived in long-term archive IDA and documented with persistent identifiers (URN) in metadata catalogue Etsin to improve the discoverability of the data. Data collected in short-term campaigns employ the same storage infrastructure and are archived in IDA. In case of continuous measurements outside SMEAR stations, scheduled copying of data to the storage servers is set up, backed up regularly and write access is restricted to few technicians and data managers to ensure security.

The climate modelling workflow is managed entirely under CSC infrastructure. Climate modelling groups utilize the Sisu and Taito HPC infrastructure for model simulations, and CSC data infrastructure AVAA, IDA and Etsin. The international Earth System Grid Federation (ESGF) infrastructure will be used to publish and acquire climate model simulation data (CMIP6) through upcoming national ESGF node at CSC implemented in Pouta virtual environment. The Earth System model data is centrally stored in dedicated CSC storage to ensure common access to all INAR groups. Climate model output is timely postprocessed into manageable size range and stored with metadata in IDA, CSC HPC Archive, or later in ESGF.

The primary data repository for end-users is SMEAR database where about 1500 environmental variables measured more or less continuously at SMEAR stations are currently available. The data are accessible via AVAA SmartSMEAR browser user interface (https://avaa.tdata.fi/web/smart/smear) and Application Programming Interface (API, documentation at https://avaa.tdata.fi/web/smart/api). Open access is favored when publishing the result articles.

RESEARCH COLLABORATION

The extent of our international collaboration is vast in the areas of research, research infrastructures, innovations and education, including over 137 active collaborators. The CoE ATM predominantly acts as a coordinating body in the research activities taking the lead in directing the science, e.g. within ICOS, ACTRIS, eLTER, AnaEE, PEEX and Future Earth.

CoE ATM is also a key partner in the CLOUD consortium at CERN, Geneva, providing state of the art instruments, such as API-TOF-MS and CI-API-TOF-MS, for molecular measurement of particle
formation, NAIS for ions size distributions, and PSM instruments for measuring aerosol formation rate at size as small as 1 nm. CoE ATM has participated to all the CLOUD campaigns, elucidating several new particle formation mechanisms. CoE ATM is also involved in the cloud and ice formation CLOUD experimental part.

The link from the ATM scientific breakthroughs towards innovations is established via a close co-operation with SMEs, especially with Airmodus Ltd., Karsa Ltd. and SMEAR Ltd. that are university spin off companies. Furthermore, Finnish Meteorological Institute and University of Helsinki have a strategic partnership with e.g. Vaisala Ltd. University of Helsinki and Finnish Meteorological Institute are partners in Cluster for Energy and Environment research consortium, CLEEN Ltd and contribute to the CLEEN research programs.

INAR Finland collaborates closely with CSC - IT Center for Sciences. CSC has long-standing collaboration with INAR Finland research community in the work done in the CoE ATM and it has been involved in INAR RI and INAR RI Ecosystems projects. Collaboration includes computing platform and data infrastructure development: dedicated support person located on-site in UH 2-3 days a week, support provided for software performance and installing, developing and running atmospheric science models (ESM, micro-meteorology, climate, atmospheric chemistry and physics) and related post-processing of results, acquired hardware to Taito cluster and Pouta cloud platform to support atmospheric science, and development and provision of Smart SMEAR web portal for easy and open data access.

In the beginning of 2017, the UEF team have been strengthened by a Biogeochemistry group (http://www.uef.fi/en/web/bgc), thus merging the approaches previously developed in UH/For in soil biogeochemistry and the UEF aerosol team into a new, multidisciplinary component in CoE ATM. The group led by newly appointed Professor Jukka Pumpanen studies the processes underlying GHG fluxes between ecosystems and the atmosphere and focuses on the response of the fluxes to climate and land use change. They contribute to Tasks 2.4 “Production of aerosol precursors by biosphere processes in various environments” and 2.5 “Atmospheric turbulence, fluxes of clusters, GHGs, BVOCs, amines, sulfur compounds, oxidants, HONO, COS” in the CoE ATM research plan. The research focus of UEF aerosol group is on aerosol-cloud interaction studies and on investigations of anthropogenic-biogenic interactions related to atmospheric secondary products formation. Hence the new Biogeochemistry group in UEF team will strengthen the multidisciplinary aspects and open new research possibilities at UEF.

INAR FINLAND

An important factor behind the success of the CoE ATM is the long-lasting, multidisciplinary collaboration between the Universities of Helsinki, Finnish Meteorological Institute and University of Eastern Finland, and between the physics, chemistry, forest sciences and environmental sciences departments in UH (Fig. 2). This research community has been fulfilled with Tampere University of Technology in recent years especially regarding collaboration in research infrastructures, and UH, FMI, UEF and TUT signed 10.1.2013 a contract to establish a national Institute for atmospheric and Earth system research (Ilmakehätutkimuksen keskus). It is a network that is led from the Division of Atmospheric Sciences, Department of Physics at UH.
INAR Institute will be its own department at UH as the division of Atmospheric sciences will be terminated starting from 1.1.2018. Also national INAR Finland is led from INAR Institute at UH. The rector of UH has established INAR Institute (30.5.2017) as a joint unit under the Faculties of Science and Agriculture and Forestry starting 1.1.2018. Joint INAR steering committee between these two faculties has been nominated at UH and the faculties negotiate the budget of INAR Institute with the rector. INAR steering committee is responsible for budget guidance. The steering committee suggests and rector nominates a leader for INAR Institute for a 5-year-term. The leader develops the institute, promotes research and education in atmospheric and Earth system sciences, promotes active collaboration between INAR partners, and develops multidisciplinary, international collaboration within the unit. The leader prepares and presents an annual action plan for the INAR council and is responsible for the usage of budget directed for INAR Institute within UH. The leader nominates an executive committee at UH with representatives of different scientific fields and education to plan and direct INAR Institute within UH and to prepare, enforce and coordinate activities for the national INAR Finland.

The negotiations of the structure and regulations of INAR Finland at national level are ongoing national contract between host-organizations will be rewritten next year. The long-term aim is that INAR Finland would be a pilot of a national research unit with own budget responsibility that would allow INAR Finland to be a partner in international projects and networks. The planned structure for national INAR Finland is such that there is a national INAR board and national INAR advisory committee both with representatives from all host organizations. INAR board would be responsible on strategic planning, decide national budget, accept the yearly action report and nominate the scientific advisory board for INAR Finland (see below). INAR board would consist of vice-rectors or deans and meet once or twice a year. National INAR advisory committee would meet more often and consist of research PI:s that can plan and develop joint research, research infrastructure and education. To evaluate the strategy, planning and activities of INAR
Finland, an international Scientific Advisory Board will be nominated by national INAR board consisting of min. 50% of foreign experts in the scientific fields and technologies represented in INAR Institute.

INAR Finland is the national focal point of ESFIs ICOS, ACTRIS, AnaEE and eLTER. This research infrastructure community, INAR RI, is broader than INAR Finland, is coordinated by Infrastructure Advisory Board. The Infrastructure Advisory Board has representatives from all host organizations involved in ICOS Finland, ACTRIS Finland and INAR RI Ecosystems. The Infrastructure Advisory Board will prepare RI-related issues for the Board of RI funders (ministries), and together with the INAR Institute leader for the National INAR Board. The scientific advisory board will be joint for INAR Finland and INAR RI.

RESEARCH HIGHLIGHTS

Five of our researchers have been selected as Thomson Reuters Highly Cited Researchers 2016: Markku Kulmala, Douglas Worsnop, Veli-Matti Kerminen, Tuukka Petäjä and Ari Laaksonen. The list includes a total of 16 researchers from Finland from all disciplines.


Research highlights of the CoE ATM for the past year covers various temporal and spatial scales (references for all bullet points can be found from the group and research abstracts from this issue):

- Studies in Antarctica were made during 2014-2015 summer season and in Ny Ålesund, Svalbard, spring/summer 2017, and at both sites we have now revealed the exact molecular steps in cluster and new particle formation.
As a side product of our atmospheric research, and especially that related to instrument development, we found means for extremely sensitive explosive trace detection (ETD), from which a new commercial spin-off company, Karsa ltd. was established in 2016.

First systematical study reveals fragmentation of sulphuric acid clusters in an Api-TOF mass spectrometer.

Quantum chemical studies suggests that a large spectrum of amines have the potential to be involved in atmospheric particle formation.

Simulations show that surface geometry alone does not predict the effectiveness of an aerosol particle to act as an ice nucleation seed.

Reliable observations of the physical properties of aerosol particles were provided for gaining new understanding of processes related to new particle formation (NPF), particle growth and cloud droplet formation.

Collection and analysis of the first global data set of sub-3nm particle concentrations (Kontkanen et al. 2017) and a better understanding of the role of photochemistry and other environmental variables in formation of clusters and new particles in the atmosphere (Jokinen et al. 2017, Kontkanen et al. 2017, Dada et al. 2017). Additionally, new experimental approaches (e.g. Steiner et al. 2017, Wagner et al. 2017, Kangaslouma et al. 2017) have made it possible to study e.g. recombination, ion-induced nucleation, and decrease the uncertainties (see Kangaslouma and Kontkanen et al. 2017) in sub-10 nm particle detection.

Particle growth rate from below 10 nanometers to accumulation mode was shown to increase with increasing particle diameter and temperature.

The importance of biological and anthropogenic activities on new particle formation (NPF) occurrence was shown: moth infection increased the NPF event frequency by increasing the biogenic vapor emissions in a model study, and the NPF event frequency was extremely high at a measurement site at the western coast of Saudi-Arabia, when the air masses passed over areas with strong anthropogenic sulphur emissions.

Concentrations of sub-3 nm particle at nine locations around the world were presented, and by comparing their spatial and temporal variations it was shown that both anthropogenic and biogenic emissions have significant impacts on their concentrations.

We have developed a chemical mechanism to simulate the formation of highly oxygenated molecules (HOM) based on the reaction of monoterpenes (e.g. Alpha-pinene) with ozone and/or the hydroxyl radical. First results of the application of the new code at different measurement stations show a crucial contribution of HOM to the growth of new particles in the size range 1-10 nm and an overall participation to the fine-mode aerosols between 10-50 % (Huang et al. 2016, Öström et al. 2017).

Correctly accounting for aerosol-cloud interactions will significantly improve the ability of numerical weather prediction models to forecast fog episodes.

Model simulations in combination with satellite observations show that although anthropogenic aerosol dominates the global radiative aerosol effect, the aerosol forcing resulting from temperature dependent emissions of biogenic sources can become more significant in the warmer future climate.

We have measured OH reactivity in ambient air in boreal forest during spring and summer 2016 together with various BVOCs. Our ambient concentrations do not explain the measured reactivity.

Forest floor is an important BVOC source.

Proton transfer reaction time of flight (PTR-TOF) mass spectrometers together with in-situ gas chromatographs/mass-spectrometers form a powerful tool for analyzing fluxes and species specific concentrations of various VOCs and oxygenated compounds.

Revised hygroscopicity of sea salt aerosol particles leads to a reduction in aerosol-radiation interactions in global model simulations (Zieger et al. 2017).

Our study demonstrates that in monoterpene dominated environment in atmospherically relevant conditions, the effect of particle phase diffusion limitation on partitioning of organic vapors is minor (Yli-Juuti et al. 2017).
• We show that secondary organic aerosol yields from Scots pines are controlled by a complex terpene profile of emissions (Faiola et al., to be submitted).
• First systematic study reveals fragmentation of sulphuric acid clusters in an Api-TOF mass spectrometer.
• Quantum chemical studies suggests that a large spectrum of amines have the potential to be involved in atmospheric particle formation (Elm et al. 2017, Olenius et al. 2017).
• Simulations show that surface geometry alone does not predict the effectiveness of an aerosol particle to act as an ice nucleation seed.
• For α-pinene ozonolysis, flow-tube reactor experiments revealed the enhancement in new particle formation and secondary organic aerosol formation in presence of dimethyl amine, and some of these N-containing reaction products were also observed in atmospheric aerosols collected at the SMEARII station (Duporté et al. 2016, Duporté et al. 2017)
• Soil chamber samples were successfully collected using solid-phase microextraction (SPME) fiber; portable gas chromatography-mass spectrometry analysis showed that the most abundant BVOCs measured were monoterpenes α-pinene and δ3-carene (also the amounts of aliphatic aldehydes were measured and were shown to be lower in soil chambers than in ambient air) (Barreira et al. 2017a).
• A significant improvement on static and dynamic sampling capacity of BVOCs from boreal forest was observed with a new SPME arrow system when compared to SPME fibers, with collected amounts approximately 2 times higher for monoterpenes and 7-8 times higher for aldehydes (Barreira et al. 2017b).
• Liquid chromatography-tandem mass spectrometry, spectrophotometry and QPCR analyses of atmospheric aerosols revealed clear annual patterns of bioaerosol components: elevated levels for free amino acids and bacteria were observed during the pollen season in SMEAR II station (~77% of total pm may be of biological origin), whereas highest abundances for fungi were observed in autumn (bioaerosols were accumulated in the size fraction of 2.5-10 μm) (Helin et al. 2017).
• Warmer winters were found to have a drastic impact on the hydrological cycle in urban environment with increase both in total surface runoff as well as in peak runoff intensities (Järvi et al. 2017)
• CH₄ and CO₂ fluxes measured over a lake using different techniques (eddy covariance, floating chambers, and direct measurements of water turbulence and gas transfer coefficient k) agreed with each other and recent parameterizations for k by Heiskanen et al. (2014) was superior in comparison with more simple ones (Erkkilä et al. 2017, see also Heiskanen et al. 2014)
• Theoretical analysis indicates that the reduction in vapour pressures of water and CO₂ in leaves due the Kelvin effect (curvature of mesophyll-air interface) could enhance plant water use efficiency up to about 10 % at a leaf water potential of -2 MPa, and much more when water potential decreases further (Vesala et al. 2017)
• Comprehensive measurements on ecophysiological processes, their seasonal dynamics and variations due to a variety of stresses were performed in field and laboratory conditions (Köster et al. 2017, Mäki et al. 2016, Schiestl-Aalto et al. 2017)
• We developed models for tree and forest ecosystem structure and functioning at sub-leaf scale, stand scale and region/continental scale, accounting for our detailed process understanding and tested with long-term datasets (Atherton et al. 2017, Hari et al. 2017, Kalliokoski et al. 2016, Mäkelä et al. 2016, Minunno et al. 2016).
• By analysing radiosonde soundings and satellite precipitation data we determined a new mechanism to explain the relationship between deep convection and lower tropospheric humidity.
• We have developed algorithmic parameter estimation techniques, foremost the ensemble prediction and parameter estimation system (EPPES) which has proven to shift the effort of model tuning from human learning to expert assisted machine learning.
• Our idealised numerical experiments have shown that extra-tropical cyclones are more sensitive to the lower-tropospheric temperature gradient, which is predicted to decrease in the future, than the upper-level temperature gradient which is predicted to increase and that the structure of the most extreme extra-tropical cyclones changes when the mean temperature is increased.

NEW PROJECTS

Academy professor Markku Kulmala received ERC Advanced Grant –funding in spring 2017 to study Atmospheric Gas-to-Particle Conversion, and Dr. Mikko Sipilä ERC starting grant to study how aerosol particles are formed from atmospheric gases. Dr. Mari Pihlatie received ERC starting grant in autumn 2017 to measure and model methane emissions from trees.

We have received EU infrastructure funding for ACTRIS PPP (Aerosols, Clouds, and Trace gases Research Infrastructure), eLTER (European Long-term Ecosystem Research), ENVRI PLUS H2020 project (European initiative for common development of major environmental research infrastructures in Europe), RISCAPE (examining the international landscape of research infrastructures, evaluating non-European research facilities and networks outside of Europe) as well as EOSC pilot (European Open Science Cloud). We are leading European iCUPE project as part of larger ERA Planet project aiming to strengthen the European Research Area in the domain of Earth Observation towards integrative and comprehensive understanding on polar environments.

The Academy of Finland has granted €15 million to the University of Helsinki in the third round of research profile funding. The grant is intended to fund 25 tenure track positions and their starter packages for three profile areas: Atmospheric and Earth system science (INAR Institute), Data science and Sustainability science. For INAR Institute,

We have received new Academy funding for research infrastructure via ACTRIS Finland and INAR Ecosystems. INAR Ecosystems is led by prof. Jaana Bäck and has as collaborative partners Natural Researches Institute Finland, Finnish Environment Institute, Universities of Eastern Finland, Oulu, Turku and Jyväskylä. This funding will strengthen national collaboration in ecosystem research.

EMME-CARE proposal got through the first Teaming Phase of H2020 CSA call. EMME-CARE proposes the establishment of a world-class Climate and Atmosphere Research and innovation Centre focused on environmental challenges at the Eastern Mediterranean and Middle East region through a combination of research, innovation and education. CoE ATM leads the research infrastructure and education parts of the project.

HAZE Beijing project is a joint project between CoE ATM (coordinated by UH) and Beijing University of Chemical Technology (BUCT) funded by Beijing Municipality Government to understand chemical processes behind the haze phenomenon. For the smooth operation of the project a new Department of Atmospheric Sciences is established in BUCT together with UH. HAZE Beijing research activity is based on SMEAR measurement concept and is part of Global SMEAR network. The total budget of the project is 19.5 MEuro.

Prof. Hannele Korhonen was among three recipients of a 5 Million US dollar grant by the UAE Rain Enhancement Program for her work on the role of atmospheric aerosols.

The Faculty of Science has awarded 3.2M € funding over a 4-year period to the collaboration project ATMATH (Atmospheric Mathematics). The collaboration involves mathematicians and atmospheric scientists. The project principal investigators are prof. Hanna Vehkamäki, Academy prof. Timo Vesala, Academy prof. Antti Kupiainen and Academy prof. Matti Lassas. The aim of the ATMATH project is to develop mathematical methods used in atmospheric science and apply them to concrete problems of atmospheric research.
Academy of Finland has granted research funding for two research fellows, two post-doctoral researchers and two consortiums: Arnaud Praplan (research fellow) for studying reactivity of forest air and tree emissions, Harri Kokkola (research fellow) for studying the role of native and anthropogenic aerosols for climate effects, Ditte Taipale (post doc) for comprehensive atmosphere-ecosystem simulations to develop climate change scenarios, Anna Lintunen (post doc) for studying the role of bark permeability in tree performance and survival in changing climate, Annalea Lohila (in consortium) for studying the contribution of upland forest soils in the regional methane balance from local to global scales, and Miikka Dal Maso and Mikko Sipilä (in consortium) for studying direct atmospheric cluster formation in various environments with consistent and mobile instrumentation. Also, two of our researchers got new key project funding (“kärkihanke”) from the Academy of Finland: Dmitri Moisseev on weather radar network in Helsinki, and Albert Porcar-Castell on effective methods to evaluate viability and productivity of vegetation in larger scale.

OTHER OUTCOMES

Members of the CoE ATM have received numerous awards during the past year. Academy Professor M. Kulmala was awarded the honorary title of Academician of Science, the highest honour that can be bestowed on any individual scientist in Finland, the honorary title of The World Academy of Sciences fellow, and he was appointed as professor of honour for his achievements in atmospheric sciences in the Tjumen State University in Russia. Prof. Douglas R. Worsnop received the American Chemical Society award 2017 for Creative Advances in Environmental Science and Technology. Mikael Ehn and Mikko Sipilä received a highly appreciated Smoluchowski award 2017 for their contributions to the role of molecular reactions and cluster formation for the growth of new atmospheric particles. Chancellor Kaarle Hämeri received International Aerosol Fellow Award 2016. Federico Bianchi received the Swiss Aerosol Group Award for the best scientific publication in the field of international aerosol research written within Switzerland, and the Arne Richter Award for outstanding early career scientists from the European Geosciences Union. Prof. Kari Lehtinen received a grant of merited scientist from the Finnish Association for aerosol research.

We lead international research programmes PEEX (Pan-Eurasian Experiment), Future Earth and International Eurasian Academy of Science (IEAS) as well as national focal points in ESFRI roadmap infrastructures in the environmental domain in Finland, namely ICOS (Integrated Carbon Observation System), ACTRIS (Aerosols, Clouds, and Trace gases Research Infrastructure), eLTER (European Long-term Ecosystem Research) and AnaEE (Infrastructure for Analysis and Experimentation on Ecosystems). ICOS and ACTRIS head offices are in Finland, at Kumpula campus.

Three books related to our work has been published. Yhdessä Ilmakehässä' by Mai Allo introduces atmospheric science for the wider audience, tells about the history of SMEAR stations and our Center of Excellence, and characterizes some key researchers in a lively manner. The book was published by the Finnish Literature Society in autumn 2016 and received a highly appreciated Finnish award for spreading knowledge ‘Tiedonjulkistamispalkinto’. A cartoon book ‘Ozone diary’ (Otsonipäiväkirjat) by Dr. Tero Mielonen and cartoonist Pentti Otsamo combines atmospheric sciences and art. The main character is an atmospheric scientist Paavo who goes abroad after his doctoral defense to study ozone with satellite measurements. The book was published (in Finnish) by Ursa in autumn 2016. "Erämaa elää, metson matkassa Itä-Lapin kairoissa" by Teuvo Hietajärvi was published in autumn 2017 launched and contains amazing photographs from the nature of Värriö (SMEAR I) and its surroundings.

Sitra and teachers, experts and students from higher education institutions created an open course on the basics of climate change - Climate.now. The Climate.now course meets a clear need to educate a new generation of climate experts for all fields, one that understands the fundamentals of climate change and can apply this knowledge within their respective fields. Researcher Laura Riuttanen from CoE ATM was responsible for coordinating the creation of the course.
We celebrated 50 years anniversary of Väriö research station 17th of August in Salla, Lapland. The research station was founded in 1967 to study animals, but 25 years later the main research focus changed to study the interaction between forests and the atmosphere as SMEAR I station was built. This year some expansion was built to the measurement hut at SMEAR I. Väriö research station is jointly under the departments of physics and forest sciences.

Finland and China have given a joint announcement of collaboration during the visit of the president of China in Finland in April 2017. One goal in collaboration is joint efforts to mitigate climate change. Our CoE ATM, led by Academy prof. Markku Kulmala who is the only Finnish member of the Chinese Academy of Science have ambitious plans to build a high-level measurement station in China to identify and understand the key air pollutants in Chinese megacities. As part of this collaboration, we are building a SMEAR station to Beijing together with the Beijing University of Chemical Technology, BUCT. Collaboration contract was signed during the trip of the Prime Minister Juha Sipilä in China (Joni Kujansuu was present).

Prof. Jaana Bäck was the leading author of a report released by the European Academies’ Science Advisory Council on Managing Europe’s forests under conflicting objectives. We need joint forest policy within EU says the leading writer of the report. Also in Finland, almost 70 Finnish Forest and Atmospheric scientists have signed a statement on the climate effects of increased use of forests for bioenergy. The researchers are concerned that increased use of forests for bioenergy will warm up the climate in the next few decades. Change from fossil fuels to bioenergy will have a positive effect on climate in a longer perspective, but the next few decades are crucial in terms of climate change.

Merli Juustila, the science secretariat of Future Earth, organized a March for Science in Helsinki on 22 April 2017 to make science enthusiasts heard (launched in the United States). March for Science was initially created as a counter-attack for the Post-Truth Era. Now, people around the world want to show that they still believe in science, research and facts.

There have been 14 PhD defences during the past year.

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INTRODUCTION

As a member of the Finnish Centre of Excellence (CoE), the Atmospheric Aerosols Research Group studies natural and anthropogenic aerosol particles from both a climate and air quality point of view and their inter-linkages. The motivation is to deepen our understanding of the chain from aerosol emissions via atmospheric processing to the impacts on clouds, climate and air quality. For this, the group utilizes the latest state-of-the-art measurement devices and develops both instrumentation and data analysis algorithms.

The research can be divided into these four main topics:

• Primary and secondary aerosol sources
• Clouds and climate
• Black carbon and other light absorbing impurities
• Methods development

METHODS

1. Primary and secondary aerosol emissions

For the estimation of aerosol forcing in global climate models, as well as for various air quality applications, understanding the anthropogenic aerosol emissions and their potential processes in the atmosphere is important. We have contributed high-quality scientific emission studies from various sources. Particulate emissions from different engines (e.g. light-duty vehicles, marine, busses; Aakko-Saksa et al., 2016, Ntziachristos et al., 2016) using different fuels (e.g. ethanol, LNG, gasoline, diesel; Timonen et al, 2017, Karjalainen et al., 2017, Saarikoski et al, 2017, Alanen et al., 2017) and different after treatment systems (e.g. selective catalytic reduction (SCR), oxidation catalysts, scrubbers, diesel particulate filter (DPF); Lehtoranta et al, 2017, Saarikoski et al, 2017) were thoroughly characterized. A particular focus was on chemical characterization of primary and secondary emissions. In many cases, secondary aerosol formation potential was significantly larger than primary particulate emissions (e.g. Timonen et al., 2017, Karjalainen et al., 2016). Also, it was found that ethanol fuels for light-duty vehicles and the modern after treatment systems and alternative fuels (ethanol, liquefied natural gas (LNG); Saarikoski et al., 2017, Pirkola et al., 2016) for busses were observed to dramatically decrease both primary emissions and secondary aerosol formation potential (Timonen et al., 2017, Karjalainen et al., 2016).

Besides the emission sources, atmospheric aerosols were studied at different traffic related environments by stationary and mobile measurements (Rönkkö et al., 2017). Traffic was observed to produce large
amounts of previously unmeasured nanocluster aerosols (NCA; Rönkkö et al., 2017). For instance, in a semiurban roadside environment, the NCA represented 20–54% of the total particle number concentration in ambient air (Rönkkö et al., 2017). In addition, urban air quality was investigated by physical and chemical characterization of urban winter-time aerosols by mobile measurements in the Helsinki area (Pirjola et al., 2017). Physico-chemical properties of particles were found to vary strongly both in time and space depending on which sources dominated. Four major types of aerosol were identified in Helsinki area: 1) clean background aerosol from marine air flows from the Atlantic Ocean, 2) long-range transported (LRT) aerosol pollution due to air flows from Eastern Europe, 3) fresh smoke plumes from residential wood combustion in suburban houses, and 4) fresh emissions from traffic. Additionally, the characteristics, dynamics and sources of particulate matter in an underground mine were studied that was probably one of the most comprehensive studies examining the chemical composition and sources of particles in an underground mine to date (Saarikoski et al., 2017 submitted).

2. Aerosol-cloud interactions: in-situ and remote sensing

Poorly understood aerosol-cloud interaction processes are a major source of uncertainty in current climate sensitivity predictions. Lately, we have contributed to several studies for better understanding of particle cloud activation properties. The Pallas GAW station on top of the Sammallunturi fell has served as a site for the Pallas Cloud Experiment campaigns since 2004. Our main motivation during the campaigns has been to investigate aerosol-cloud interactions using in-situ and ground-based remote sensing techniques. In-situ cloud properties were measured by two different cloud probes installed on the roof of the station and the averaged cloud properties from several campaigns are summarized by Doulgeris et al., 2017.

On the remote sensing side, the group has further developed research using a cloud radar (Hirsikko et al., 2015), and improved the utilisation of ceilometers. Super-cooled liquid water containing clouds are frequently observed over Finland. These clouds can cause significant icing and produce precipitation which can contain ice or freezing rain droplets. However, numerical weather prediction models find it challenging to forecast such conditions. Pallas in-situ cloud observations and remote-sensing observations were supplemented with satellite overpasses. First results of such multi-scale analysis were reported in the European Geosciences Union General Assembly in Vienna (Hirsikko et al., 2017a). Additionally, we have investigated the capability of ceilometer network for near-real-time (NRT) icing condition monitoring and warning (Hirsikko et al., 2017b and 2017c). A preliminary classification scheme for icing potential of hydrometeor populations was developed based on ceilometer backscatter profile observations. A comparison with in-situ icing rate observations suggests that ceilometers can be used for NRT profile monitoring of icing conditions. These measurements are an integral part of an Aerosol, Clouds and Trace gas InfraStructure European network (ACTRIS) activities.

Finland’s remote sensing network (Hirsikko et al., 2014) is also contributing to other European activities. The group is responsible for the creation of an emerging European Doppler-lidar network which will harmonize wind and turbulence retrievals within the boundary layer (O’Connor et al., 2017a; b). To this end, new post-processing methods for Doppler lidars have been recently developed (Manninen et al., 2016). In addition we have also created a boundary layer classification which identifies sources of turbulence and whether turbulent mixing is connected to the surface and the clouds. For example, one source of turbulence is low-level jets. A low-level jet algorithm tailored for high resolution Doppler lidar data was developed and applied to over two years of Doppler lidar wind profile data from Utö, Finland (Tuononen et al., 2017). The algorithm can be used to identify low-level jets operationally and it have been applied to other Doppler lidar sites in Ireland, Germany and Finland.

3. Studies of aerosol climate forcing using long-term data

A major factor improving our understanding of climate change are the high-quality long-term aerosol observations. We are conducting continuous field measurements of aerosol chemical, physical and/or optical properties in different stations in Finland: In Pallas-Sodankylä Global Atmosphere Watch (GAW)
station (since 1996), Matorova measurement station, Utö Atmospheric and Marine Research Station, and Virolahti measurement station. The last three stations are part of the European Monitoring and Evaluation Programme (EMEP), in which we are measuring particulate organic and elemental carbon according to CAFÉ directive (2008/50/EY).

Our international activities are focused on regions that are the most highly influenced by climate change, such as the Arctic, the Antarctic, southern Africa and the South-East Asia. In India, together with The Energy and Resources Institute (TERI) we have measured a unique long-term data series (since 2005) from the foothills of Himalayas (Hooda et al., 2017). Results showed a statistical trend of -1.9 \( \mu \text{gm}^{-3} \) per year and -2.3 \( \mu \text{gm}^{-3} \) per year for particulate matter, PM2.5 and PM10, respectively. In southern Asia, the effect of monsoon rain on aerosol properties and long-term size distribution (since 2004) was studied in Maldives, showing a consistent pattern of monsoon on particle number and sizes (Kesti et al., 2017).

In collaboration with Russian Roshydromet and the Arctic and Antarctic Research Institute (AARI), and NOAA from USA, we have done all year-round aerosol observations in the Russian Arctic, Tiksi, since 2010 of which the annual patterns and sources have been recently presented (Asmi et al., 2016). In collaboration with AARI we have also started long-term measurements in a high Arctic Russian site at Cape Baranova in autumn 2015.

On the southern hemisphere, together with the University of Helsinki, we are participating in long-term measurements in South Africa recently focusing on atmospheric aerosol chemical composition (Aurela et al., 2016; Venter et al. 2016 and 2017), sources and concentrations of black carbon (Chioane et al., 2017) and the role of biomass burning aerosols in the regional aerosol load (Mafusire et al., 2016). In addition, the aerosol measurements at the Antarctic peninsula Marambio station were started in January 2013 in cooperation with Servicio Meteorologico Nacional (SMN) Argentina. This four-year data series was recently analysed for a year-round chemical composition and source contributions of aerosols (Asmi et al., 2017).

4. Black Carbon in the snow and in the atmosphere

Snow and sea ice are some of the most reflective surfaces that occur naturally. Airborne black carbon (BC) or soot, which originate from incomplete combustion, is a particularly potent absorber of solar radiation and even trace amounts can affect the reflectivity of snow and sea ice. BC has been estimated to be the second most important climate warming pollutant after carbon dioxide (e.g., Bond et al., 2013). Accurate measurements of BC in the Arctic as well as in other snow and ice covered areas is, therefore, of particular importance.

Temporal and spatial variability of BC around the Arctic was studied using the data from the stations of International Arctic Systems for Observing the Atmosphere (IASOA: www.iasoa.org, Uttal et al., 2015). The group is actively participating in IASOA expert group work, and is maintaining BC and other aerosol measurements year-round at three Arctic stations. Two significant results were recently presented based on Aethalometer measurements at six Arctic station from 2012–2014 (Backman et al., 2017). First, an alternative method of post-processing the Aethalometer data is presented that reduces measurement noise and lowers the detection limit of the instrument more effectively than boxcar averaging. Second, utilizing co-located reference methods of aerosol absorption, an Arctic specific correction factor (\( C_f \)) of 3.20 was introduced which is specific to low elevation Arctic stations. \( C_f \) is a fundamental part of most of the Aethalometer corrections available in literature. These results will both unify BC measurements in the Arctic and provide a means to measure very low, but still significant, concentrations of BC. This is the first time a \( C_f \) value has been obtained for the Arctic.

In order to estimate the climatic impact of BC, a method to measure soot particle sizes and mixing-state in the atmosphere is needed. This is currently done with a Single Particle Soot Photometer (SP2) instrument. SP2 measurements from FMI Pallas GAW station showed that soot concentrations in Finnish Lapland were low most of the year and that practically all the particles were thickly coated, thus indicating
internally mixed particles (Raatikainen et al., 2015). In contrast, the first-ever size-segregated BC measurements in northern India showed the presence of two different BC modes, suggesting towards various sources of BC (Raatikainen et al., 2017). BC also contributes to light-absorbing impurities (LAI) on snow. Svensson et al., 2017 developed a method to distinguish between BC and dust absorption within snow which was applied on samples from both Finland and the Himalayas (India). It was shown that dust, in addition to BC, can be a significant contributor to LAI especially in India (Svensson et al., 2017).

5. Instrumentation and method development

The group is also actively developing new instrumentation and scientific methods to facilitate the ongoing research. For example, the mapping of spatial distribution of particulate matter (PM) concentrations requires high resolution monitoring networks. Currently, high unit cost and complexity of the standardized monitoring instruments limits the availability of these monitoring networks. Research and development of inexpensive aerosol sensors aims to achieve better understanding on how the more affordable and simpler sensors could be used to improve spatial coverage of air quality monitoring. Results from various experiments indicate that the accuracy and other practical properties of the inexpensive sensors are promising and that significant progress can be made regarding air quality monitoring (Kuula et al., 2017).

In the field of vertical profiling of atmospheric composition, remotely piloted aircraft systems are a new promising method. The group contributed to spring ACTRIS JRA2 inter-comparison campaign in Hyytiälä field station, where measurements of the vertical exchange of aerosol particles in the boundary layer using a combination of state-of-the-art in-situ and remote-sensing techniques were conducted. In order to get a better understanding of the variation of concentrations higher up in the boundary layer at the same time with surface flux measurements, vertical profiling of aerosol particles, temperature, pressure and relative humidity was done by the FMI-RPAS (tailored hexa-copter with ground station). The FMI-RPAS operated within the reserved airspace and during the whole campaign, 29 vertical profiles were obtained with ceiling heights dependent on day-to-day weather conditions. These profiles are used to support on-site measurements, e.g. to understand particle layering within the atmosphere and to pinpoint the particle formation hot-spots.

CONCLUSIONS

A short overview of our recent activities, supporting the goals of the Finnish Centre of Excellence in Atmospheric Science – From Molecular and Biological processes to The Global Climate –program, was presented. Further research highlights will be shown in the seminar.

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Introduction and Objectives

The main aim of the Atmosphere Modelling Group is to increase our process-based understanding of biological, chemical, physical and meteorological mechanisms in the lower part of the planetary boundary layer. This includes the emissions of biogenic volatile organic compounds (BVOC) from different ecosystems and their oxidation by OH, O₃ and NOₓ. Further the group investigates the formation and growth of secondary organic aerosols (SOA) with a focus on the contribution of highly oxygenated molecules (HOM).

Methods

Our group uses a set of different models starting from the zero-dimensional box-models MALTE-BOX and ADCHAM, the one-dimensional model SOSAA, the two-dimensional model ADCHEM and the meso-to-global scale model SILAM. In addition to understand the impact of turbulence on the different processes we operate the large-eddy-simulation model (LES) ASAM. Detailed description of all models with references and applications are provided at the group website https://wiki.helsinki.fi/display/AMG/.

Results

During the last year the main emphasis of the group was (similar to last year) directed towards the further development of our mechanism to simulate the formation of HOM and to see how these molecules will contribute to the formation and growth of new particles at several selected research stations. We also implemented a new multi-layer deposition module for thousands of organic and inorganic molecules into the 1D chemistry-transport model SOSAA, validated the code for ozone deposition at SMEAR II (Zhou et al., 2016a) and investigated how important deposition impacts the concentrations of several selected molecules compared to chemistry and turbulence inside the canopy (Zhou et al., 2017b). Further we currently simulating with our one-dimensional chemistry-transport model SOSAA a period of 14 years at SMEAR to investigate the long-term trends of two oxidants (OH and NOₓ) and related molecules (e.g. HO₂, H₂SO₄, N₂O₅), which are at SMEAR II only measured for short periods.

Impact of deposition on the concentrations of emitted and formed biogenic organic compounds

We applied a multi-layer gas dry deposition model, which was developed and implemented into our 1-dimensional chemical transport model SOSAA (a model to Simulate the concentrations of Organic vapours, Sulphuric Acid and Aerosols) to calculate the dry deposition velocities for all the gas species included in the chemistry scheme (> 1000 compounds). The new model was used to analyse in-canopy sources and sinks, including gas emissions, chemical production and loss, dry deposition and turbulent transport of selected biogenic volatile organic compounds (BVOCs) at the boreal forest site SMEAR II.
This study has shown that dry deposition of oxidation products of precursor gases as well as other BVOCs could be a potentially important feature of improving our understanding and quantification of BVOC exchange. However, such assessments are largely limited by available observations that could further corroborate the correctness of the simulated deposition processes as presented in this study. In addition, this study stresses the necessity of applying a canopy exchange modelling system for a detailed analysis of BVOCs exchange regimes within and above a boreal forest canopy, instead of applying a big-leaf representation without considering the interactions between chemistry, emissions and deposition (see also abstract submitted by Putian Zhou).

Long-term trends of the most important oxidants at SMEAR II

We applied SOSAA with the new deposition module and detailed chemistry for long-term studies (14 years). The oxidation capacity of the atmosphere depends beside ozone and possible contributions of (stabilized) Criegee Intermediates (not well quantified) mainly on two radicals, which are responsible to sweep out all anthropogenic and biogenic emitted pollutants by chemical degradation. The hydroxyl (OH) and the nitrate radical (NO$_3$) in this way control the air quality in the lower part of the troposphere. OH is also the main sink for methane, the second most important greenhouse gas, and is involved in the formation of secondary aerosol particles over the chemical production of sulphuric acid and the chemical production of highly oxygenated molecules. Related to the cost-intensive measurements there exist no long-term trends for both of these radicals at the SMEAR II and up to our knowledge at any Nordic country. First results of our simulations show a decrease of NO$_3$ and an increase in OH. The drop in NO$_3$ radicals is partly related to a decline of mono-nitrogen oxides (NO and NO$_2$). NO and NO$_2$ reveal a strong anthropogenic footprint and are related to air quality and health problems, which caused in the last decades many efforts in cutting down their emissions from human activities. The increase in OH is related to different factors and are currently analysed.

Highly Oxygenated Molecules (HOM) and their contribution to the growth of SOA

During recent years new novel measurement techniques have been developed, which enables detection of VOC and the reaction products in the atmosphere. With these techniques Ehn et al. (2014) were able to measure rapid formation of highly oxygenated molecules (HOM) at high yields after the initial oxidation of several monoterpenes. Based on the work by Ehn and co-workers we developed (up to our knowledge) the first HOM autooxidation mechanism for monoterpenes. The new developed peroxy radical autooxidation mechanism (PRAM) for production of HOM from ozonolysis of monoterpenes with endocyclic double bonds consists of 648 reactions and 63 compounds. We coupled the mechanism to the Master Chemical Mechanism version 3.3.1 (MCMv3.3.1) and using the Kinetic PreProcessor (KPP) to get the Fortran code.

Lately HOM formed from monoterpene have been assumed to be ELVOC with vapour pressures below $10^{-9}$ Pa ($\approx 2.5 \times 10^5$ molecules cm$^{-3}$). We recently published a paper (Kurten et al., 2016) where we compared the HOM vapour pressures derived with two different functional group contribution methods and with the quantum-chemistry continuum solvent model (COSMO-RS). All functional group contribution methods indicate that most HOMs with more than 7 oxygen molecules indeed are Low Volatility Organic Compounds (LVOC) at room temperature, but the vapour pressures are too high to quantify them as ELVOC. COSMO-RS gave even higher vapour pressures, which probably can be attributed to intra-molecular hydrogen bonds.

Figure 1 shows results from an $\alpha$-pinene ozonolysis experiments in the Jülich Plant Atmosphere Chamber (JPAC). Figure (a) compares the total modelled and measured HOM gas phase concentrations changes when the $\alpha$-pinene + O3 reaction rate increases and figure (b) provides the HOM dimer concentration change.
We then applied PRAM to investigate the processes behind observed new particle formation (NPF) events and subsequent organic-dominated particle growth at the Pallas Atmosphere-Ecosystem Supersite in Northern Finland with the one-dimensional column trajectory model ADCHEM (Öström et al., 2017). The results showed that the modelled sub-micron particle mass is up to \( \sim 75\% \) composed of SOA formed from HOMs with low or extremely low volatility. In the model the newly formed particles with an initial diameter of 1.5 nm reach a diameter of 7 nm about 2 h earlier than what is typically observed at the station. This is an indication that the model tends to overestimate the initial particle growth. In contrast, the modelled particle growth to CCN size ranges (> 50 nm in diameter) seems to be underestimated because the increase in the concentration of particles above 50 nm in diameter typically occurs several hours later compared to the observations. Due to the high fraction of HOMs in the modelled particles, the oxygen-to-carbon (O:C) atomic ratio of the SOA is nearly 1. This unusually high O:C and the discrepancy between the modelled and observed particle growth might be explained by the fact that the model does not consider any particle-phase reactions involving semi-volatile organic compounds with relatively low O:C.

Figure 2 shows the mean mass fraction of each compound type that contributes to the growth during the 10 selected event days.

\[ \text{Figure 1: Modelled and measured (a) HOM(g) concentration and (b) HOM(g) dimer mole fraction as a function of the } \alpha\text{-pinene } + \text{O}_3 \text{ reaction rate in the JPAC chamber} \]

\[ \text{Figure 2: Mean mass fractions of each compound type that contributes to the growth of the particles during all chosen new particle formation events} (\text{Figure 7 from Öström et al., 2017}) \]
SUMMARY, OUTLOOK AND REMARKS

As mentioned above the main activities in the group are directed towards the development of the new and unique PRAM mechanism. This mechanism is able to realistically reproduce the observed influence of NO on the HOM composition and the observed SOA formation during ozonolysis of α-pinene in the JPAC reaction chamber. The HOM mechanism has been implemented into the process-based chemistry transport model ADCHEM and with the new HOM mechanism the model can explain the observed new particle activation and growth from 1 nm to ~20 nm in diameter over the boreal forest. But the model still underestimates the particle growth from ~20 nm to the typical lower CCN size range of around 80 nm in diameter. By considering heterogeneous oligomerization involving HOM and other organic molecules we found substantially better agreement between the modelled and measured SOA and HOM(g) concentrations in the JPAC smog chamber. We are currently evaluating the potential contribution of heterogeneous oligomerization for the new particle growth into the CCN size range.

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The Ecosystem processes – team in the ATM Center of Excellence concentrates on the ecosystems’ role in climate change. Our main results are highlighted in the FCoE Abstract Book. Most of the activities link to other themes as well, and only a brief summary is presented here.

The main aim has been to utilize the long-term measurements for building up a comprehensive understanding of the feedbacks and linkages between different compartments in the boreal ecosystems and the environment. In addition, short-term targeted campaigns, either in field or laboratory conditions, with variations of the driving forces, are used to pinpoint the key processes that need to be taken into account for model analysis and forecasting of the system changes.

Here some of the recent results are summarized under six sub-themes: Exchange of VOCs between ecosystems and atmosphere, Whole tree physiology, Optics of photosynthesis, Biogeochemical cycles, soil processes and element budgets, Forest modeling and Societal impact.

1. EXCHANGE OF VOCs BETWEEN ECOSYSTEMS AND ATMOSPHERE

For already a decade, we have been utilizing the PTR-MS technique for measuring the emissions and concentrations of VOCs in forest stand both in small scale using enclosures, and in ecosystem scale with micrometeorological methods. Part of the work has been dealing with developing and optimizing the operations of field instrumentation, including various types of measurement chambers which enclose a confined part of ecosystem under observation, and enables the detailed analysis of dynamic features of gas exchange, including both inert GHGs and the reactive gases such as VOCs (Aalto et al this issue).

The production of biogenic volatiles competes with the carbon assimilated and the emissions participate in atmospheric reactivity. The biogenic aerosol precursors contribute to aerosol formation processes, and our aim has been to quantify the magnitude of their production and exchange between boreal ecosystems and...
atmosphere, to analyse key drivers for their emissions and this way aim at improving model parameterisations.

Transpiration regulates the emissions of water-soluble short-chained OVOCs in Scots pine (Rissanen et al)

The models on plant emitted volatile organic compounds (VOCs) are mainly based on temperature and/or light, and typically contain no other physiological controls. However, the short-chained oxygenated volatile organic compounds (OVOCs), such as methanol, acetone and acetaldehyde, are soluble to water which implies that stomatal control may possibly regulate their emissions from leaves. We studied the roles and interactions of temperature, stomatal conductance and transpiration in explaining methanol, acetone and acetaldehyde emissions from Scots pine using our long term field measurements with PTR-MS. The large dataset showed that methanol emissions from pine shoots could be best explained by temperature, whereas the acetone and acetaldehyde emissions correlated well with transpiration. Stomatal conductance alone explained the emissions very poorly. We will continue the analysis in order to formulate a physiologically justified emission mode for these water-soluble compounds.

Seasonal and annual dynamics of VOC emissions from boreal forest soil (Mäki et al)

Boreal forest floor contributes from few percent to ten percent of the boreal forest VOC exchange depending on the season (Aaltonen et al., 2013), by emitting oxygenated VOCs, isoprene and monoterpenes, and also highly reactive sesquiterpenes (Mäki et al., 2017). Organic soil is found to be a significant VOC source due to high organic carbon (SOC) content (Wiesmeier et al., 2014; Ostrowska and Grazyna, 2015) and plant litter, which contains easily decomposable substrates for microbial processes. Wintertime VOC concentrations in soil and snow can be relatively high (Aaltonen et al., 2012) due to microbial decomposition processes, active even close to zero temperatures. In our measurements, high concentrations of monoterpenes were measured in different layers of the soil profile, highest in organic soil as expected (36 µg m-3), whereas sesquiterpene concentrations did not vary much with depth, indicating that their sources are more stable. The sesquiterpene concentrations and forest floor fluxes were relatively high during spring whereas highest monoterpane concentrations were measured in late summer and in fall.

Chemodiversity in Scots pine branch isoprenoid emissions as measured with portable gas chromatography-mass spectrometry (Barreira et al)

The most abundant BVOCs emitted by terrestrial vegetation are the volatile isoprenoids, including isoprene, monoterpenes and sesquiterpenes. The chemical structure of these compounds confers them distinct kinetics of reaction with atmospheric oxidants, such as O₃, OH and NO₃, that can range from seconds to days. Due to the structural diversity of isoprenoids, the photo-oxidation of these compounds will result in very distinct primary oxidation products that can contribute to secondary organic aerosol (SOA) formation and growth through gas-to-particle conversion. In addition to their structural and chemical diversity when reacting in the atmosphere, the sources of these compounds, i.e. the biogenic emissions of VOCs also possess remarkable variability, both in quantity and quality. Emission rates are reported to vary with several magnitudes, depending e.g. on plant species, season, and in particular on environment, mainly temperature and light availability. Here, we set up measurements for testing whether the emissions of monoterpenes in springtime have some qualitative patterns (i.e. chemodiversity) that can be related to the previously reported emission peaks (Aalto et al 2015) and linked to photosynthetic recovery.

Do biotic plant stresses induce formation and growth of new particles? (Taipale et al)

Climate change is forecasted to increase biotic stresses in ecosystems, and the consequence is higher emissions of volatile compounds from wounded vegetation. We constructed a model to simulate new particle formation and growth in various broadleafed forest stands under stressed and non-stressed conditions. The results indicate that not all stresses lead to new particle formation, but that some do, and then the induction is tremendous. Since plants often experience some degree of stress, and since our
study shows that individual stresses have highly different potentials to form new particles, it is crucial to measure the stressed emission caused by other major stressors.

**Emissions of volatiles from mature birch trees (Bäck, Taipale et al)**

Currently it is acknowledged that conifers such as Scots pine and Norway spruce are important sources for volatile organic compounds (VOCs) throughout the year, although the strong temperature relationships implies that emissions are highest in summertime. However, the dynamics of the deciduous birch foliage VOC emissions and their relationship with environmental drivers during the development, maturation and senescence of foliage has not been well analyzed. We measured the branch level VOC emissions from a mature Silver birch with PTR-MS during 2014 and 2015 at the SMEAR II station. The Silver birch foliage was a huge source for both short-chained volatiles such as methanol, acetaldehyde and acetone, as well as for monoterpenes. The mean emission rates from birch leaves were 5 to 10 times higher than the corresponding emissions from Scots pine shoots. However, the deciduous leaf growth dynamics affects strongly the whole canopy emission rates. We compared several semi-empirical model approaches for determining the birch foliage monoterpene standardized emission potentials, and utilized the continuous emission measurements from the two growing seasons for development of a novel algorithm which accounts for the leaf development and senescence in addition to prevailing temperature and light conditions. With these improvements and inputs to the 1D biosphere-atmosphere model SOSAA (model to Simulate Organic vapours, Sulphuric Acid and Aerosols), we showed that the maximum OH reactivity due to birch monoterpene emissions is in the range of 4-5 s⁻¹. We conclude that accounting for deciduous foliage emissions would significantly improve biosphere-atmosphere models describing the surface-atmosphere exchange of reactive gases.

### 2. WHOLE TREE PHYSIOLOGY

We study whole tree ecophysiology; how different processes in a tree are connected to each other and how they are dependent on tree functional and structural properties and environmental conditions. We focus on interconnections with xylem and phloem transport, stomatal control, photosynthesis, cambial growth, and other sink processes in varying environmental conditions. An important tool utilized is the whole stem and xylem diameter change measurements as they can used in field conditions to measure xylem and phloem water and osmotic status, which in turn, are tightly linked to source and sink water and osmotic status.

**Low apoplastic water potential in trees - Dehydration stress on living cells and embolism in xylem (Lindfors)**

Low apoplastic water potentials can affect trees by decreasing water conductivity of xylem due to embolism and by causing dehydration stress on living cells. Low apoplastic water potentials can either be caused by loss of water due to transpiration or by freezing due to chemical properties of ice formed in the apoplastic space. In his thesis, Lindfors showed that increase in gas pressure in xylem conduits can have a positive effect on tree water relations, formation of embolism in trees can temporarily even help to relieve water stress in trees, the role of living parenchyma cells in xylem diameter changes is much more significant than thought before, and that the rapid depression of photosynthesis during freezing was confirmed to be caused by dehydration stress in the mesophyll cells.

**Belowground hydraulic conductance in mature Scots pine is linked to soil temperature, soil water content and stomatal conductance in boreal environment (Lintunen et al.)**

The method of estimating belowground hydraulic conductance (\(k_{bg}\)) from simultaneous field measurements of sap flow and xylem diameter change gave reasonable results over the period chosen in terms of consistency of the time series of \(k_{bg}\) over the season between years and trees, and dependency of \(k_{bg}\) on soil temperature and soil water content. \(k_{bg}\) increased with increasing soil temperature, especially in spring when soil temperatures were cold. \(k_{bg}\) increased also with increasing soil water content if soil temperature was high enough as was the case in summer. \(k_{bg}\) was strongly linked to stomatal conductance.
Sugar accumulation in tree leaves under drought stress decreases net carbon assimilation (Salmon et al.)

Accumulation of solute and particularly non-structural carbohydrates (NSC) in tree leaves during drought has been hypothesized to decrease carbon assimilation by increasing non-photosynthetic limitation to photosynthesis. We tested this hypothesis by conducting a lethal drought experiment on seedlings of four species: *Pinus sylvestris*, *Picea abies*, *Betula pendula* and *Populus tremula*. In parallel to stomatal closure to limit water loss, we observed that an increase in leaf osmolality - used as a proxy for NSC – was related to an increase of non-stomatal limitation to photosynthesis. Our results further suggest that disruption in phloem ability to export NSC might be one of the underlying mechanisms for this accumulation of sugars.

Birch ability to refill xylem under tension (Salmon et al.)

In the context of reported drought-induced mortality worldwide, the mechanisms allowing trees to cope with drought-induced physiological damage and particularly with embolism are receiving increasing attention. One of the big unknowns is the potential for trees to refill embolised xylem during the growing season and particularly to do so under tension. Birch is known for its ability to refill winter embolised vessels prior to budburst in the so-called “sap season” in spring, we investigated if this ability is maintained through the growing season and if this can be achieved under tension. Our results suggest that birches cut branches can refill through the year, even under small tension, and that phloem unloading is likely involved in the process.

Water relations in silver birch during the birch sap exudation period (Dominguez et al)

We have measured the water relations of Silver birch during the sap exudation period in Tohmajärvi and Hyrylä during 2014 to 2016. The relationship between the changes in xylem diameter and the changes in temperature increase after bud burst. Before that, there are some periods where the xylem diameter increases beside temperature also increases. We hypothesize that increases in temperature speed up active metabolic processes in parenchyma cells, consequently releasing water into xylem vessels and increasing their pressure.

How a pathogenic fungus breaks tree resistance? (Paljakka, Rissanen et al)

Climate change increases risks for forest damage due to biotic and abiotic stress factors such as e.g. pathogens and drought episodes. The pathogen infections – even though not initially lethal to the host – may predispose the host to drought by some yet unknown mechanisms, which often eventually kill the tree. If occurring in a large scale, such combined stresses may provide a previously unaccounted climate feedback and accelerate the warming, when the damaged forests are converted to carbon source. A currently very topical stress is manifested by *Endoconidiophora polonica*, a pathogenic blue stain fungus vectored mainly by the spruce bark beetle (*Ips typographus*), an aggressive forest pest causing widespread tree mortality and significant economic losses. Importantly, *E. polonica* causes a serious drought stress in living trees by disrupting the water and solute transport between the roots and the canopy. The physiological mechanisms how pathogenic blue stain fungi break the defenses of a tree are still unknown, though both tree physiology and fungal ecology have been studied a lot. We set up an experiment to study how blue stain fungus *E. polonica* changes the physiology of Norway spruce saplings. Our results suggest that the mechanisms how E. polonica overcomes the defense of Norway spruce are related to lowered surface tension and increased vulnerability to cavitation in xylem due to the infection. A lower surface tension of tree sap, as caused by increased concentrations of organic surfactants, decreases the ability of water columns to withstand water stress. Therefore, water stress conditions most probably help the progress of fungus infection in the tree.

Cytokinin (Wilenius, Tiusanen et al):

Cytokinin overproducing mutants of hybrid aspen have higher cambial growth rates than wild type plants. Their growth is being studied as they could potentially be harvested for biomass production. We studied the hydraulic conductivity and cavitation vulnerability of cytokinin overproducing aspen. From the preliminary results it appears that they had higher hydraulic conductance but greater vulnerability to
cavitation, suggesting that it is a tradeoff in metabolic activity and drought resistance. The emissions of isoprene and methanol were different between the transgenic and control seedlings.

**Drought experiment (Laura Nikinmaa):**

Water and carbohydrate relations of Norway Spruce seedling were studied during an artificial drought induced by decreasing the water potential of the hydroponic growth medium with PEG. The effect of decreasing water potential on leaf exchange and carbohydrate relations were less severe in comparison to what could have been expected if the seedlings would have experienced a similar decrease in actual soil water potential. This could be explained by the fact that unlike in a real drought, the hydraulic conductance in the growth medium did not change during the drought treatment.

**Kemiö – case study on drought (Samuli Koivistoinen):**

Scots pine trees in Kemiö Island, Southern Finland, have been suffering from deteriorating health such as defoliation and other drought related symptoms for approximately ten years. However, the exact reason for this symptoms have not been identified. Trees were fell down in the area, and they were inspected for insects and fungi. In addition, stem disks and branches were taken from the felled trees and their hydraulic conductivity were measured. Hydraulic conductivity of the branches was significantly lower in the defoliated trees. Also Crumenulopsis sororia and Aradus cinnamomeus were found in great numbers in the felled trees. The preliminary results indicate interact between biotic factors and drought in the deteriorating health of these trees in Kemiö island.

**An exact analytical solution to a generic photosynthesis function covering various optimization hypotheses and photosynthesis models (Mauranen et al):**

A steady-state model of photosynthesis that includes soil water status as a limiting factor for photosynthesis was further developed with promising results. The development yielded a generic photosynthesis function that can be modified to represent different metabolic optimization hypotheses and photosynthesis models, while allowing an exact analytical solution in many relevant cases. The resulting functions for stomatal control agree qualitatively with experimental results in the literature and make new predictions that can be tested empirically. Work is in progress to apply this new insight to land surface modelling.

**Dynamic variations in bark hydraulics – understanding whole tree processes and its linkage to bark hydraulic function and structure (Chan):**

The bark of the tree is complex due to its function and structure: the outer-bark acts as a protective barrier against the external environment; whereas the inner-bark is where sugar transport occurs. It is within the inner-bark that much of the dynamic bark variation occurs, which is due to sugar transport, growth and growth-related processes. In this thesis, Chan linked the variations that occurred within the inner-bark to other internal tree processes and to the external environment. These tree processes and environmental conditions that are studied, focused particularly on stem growth, its growth-related processes and source-sink relations. These included [internal processes related to] photosynthesis and stem CO2 and VOC efflux processes on one hand; and [external environment related to] light, vapour pressure deficit and temperature on the other hand.

**Model of stomatal control (Höltä et al):**

We demonstrate using a numerical model that stomatal functioning can be understood from the viewpoint of maximizing the simultaneous photosynthetic production, phloem transport, and sink sugar utilization rate. Maximizing the photosynthetic production rate using a numerical steady-state model leads to stomatal behaviour that is able to reproduce the well-known trends of stomatal behaviour in response to e.g. light, VPD, ambient CO2 concentration, soil water status, sink strength, and xylem and phloem hydraulic conductance. Our modeling results also demonstrate how the “marginal cost of water” in the unified stomatal conductance model and the optimal stomatal model could be related to plant structural and physiological traits, most importantly, the soil-to-leaf hydraulic conductance and soil moisture.
3. OPTICS OF PHOTOSYNTHESIS (Porcar-Castell et al)

The goal of the Optics of Photosynthesis Lab is to generate new understanding, and develop new methods and models, in views of establishing a quantitative connection between optical, biochemical, functional and structural plant traits. We study these connections both across space and time, from the nanoseconds and molecular level, to the seasonal and satellite pixel level.

The optical methods we use are based on hyperspectral reflectance and chlorophyll fluorescence data. Currently, our main driving scientific challenges are related to the interpretation and utilization of satellite-derived solar-induced chlorophyll fluorescence (SIF) as a proxy of GPP (Porcar-Castell et al. 2014, Sun et al. In press). In addition, we are also interested in exploring the capacity of SIF and other hyperspectral reflectance indices to track various plant physiological processes such as the dynamics in volatile organic compound emission capacity (Aalto et al. 2015).

During 2017, we have conducted a pioneering and unique multiscale campaign to co-register the spring recovery of a boreal forest at multiple scales along with the optical signals these dynamics generated, with an emphasis on chlorophyll fluorescence. In addition to the OPL and other teams from the FCoE, the FAST campaign (Fluorescence Across Space and Time) involved a large number of research teams from more than 10 different countries with diverse disciplines that ranged from molecular biology (e.g. Finnish Centre of Excellence in Molecular Biology of Primary Producers) to space research (e.g. NASA-JPL) (see abstract by Porcar-Castell et al. for further details on the campaign). In addition to this time consuming campaign, the main outcome and scientific contributions from our team are described below:

Evidence of close coupling between satellite pixel SIF and eddy covariance GPP dynamics.

We collaborated with colleagues from NASA-JPL to show that OCO-2 derived SIF was closely coupled to eddy-covariance GPP in contrasting ecosystems. The findings suggest that confounding factors such as forest structure might cancel out at larger spatial scales and a generic relationship between forest GPP dynamics and SIF might be obtained. Further studies are certain to follow. The paper is currently in press in Science (Sun et al. In Press)

Leaf morphology and within canopy light gradients explain the background spatial variability in key optical traits of a boreal forest.

Interpretation of remotely sensed data requires translating information both across space and time. In the spatial context, optical data may vary in response to both physiological factors (i.e. the variation we are interested in capturing) as well as physical and structural factors (i.e. variation that adds noise to our physiological interpretation). In this study (Atherton et al. 2017) we examined the factors that control the background variability in key leaf optical traits such as the photochemical reflectance index (PRI) or the shape and level of the fluorescence spectra. We found that SIF presents much less background variability than other reflectance based indices.

The PRI, SIF and Water Index are all able to capture the photosynthetic spring recovery of scots pine needles in a boreal forest.

Complementing the study above, which concentrated on the spatial variation in optical data, we here examined the temporal co-variation of different optical indices and their relationship with the biochemical and functional recovery of photosynthesis. The photosynthetic spring recovery in boreal ecosystems is strongly regulated by temperature which means that upon increase in temperature during spring a multitude of processes take place concomitantly. High temporal resolution is therefore the key to identify mechanisms and separate processes. In this study (Chao et al. In review) we measured photosynthesis and optical data in scots pine needles for a total of 30 times between February and July. We identify different optical proxies of the spring recovery and characterize their underlying mechanisms.

Development of new methodologies for the multiscale interpretation of fluorescence data.

The OPL has been very active in filling methodological gaps for measuring and interpreting fluorescence data. During the last year we have been working in developing four different methods: a) a new spectral
chamber that, in addition to reflectance, allows us to measure the fluorescence spectra of leaves both at ambient and 77K temperature. Measurements at 77K temperature are especially informative because they tell us on the structural re-arrangements of the photosynthetic apparatus as well as the seasonal variation in photosystem stoichiometry (See abstract by Rajewicz et al.).

b) New methods for the estimation of the photosystem I (PSI) contribution to the total fluorescence signal. In contrast to photosystem II (PSII), PSI fluorescence is known to remain constant at least over the short term. However, its spatial and temporal variation remain unknown. In Porcar-Castell et al. (to be submitted) we present a new method to retrieve this contribution and test it against three independent sources of data. c) The fluorescence spectra of leaves can be measured relatively easy both in the lab and in the field using clips equipped with optical filters. Importantly, for interpretation of remotely sensed data, we are also interested in quantifying the fluorescence spectra of canopies, in addition to leaves. Canopy fluorescence spectra has not been measured before. This year (see abstract by Atherton et al.) we came out with a new and artistic solution to measure the fluorescence spectra of whole tree canopies using powerful and colourful LED lights.

d) Upscaling optical signals from the leaf to the canopy requires the use of radiative transfer models. As pointed out above (see point 2), structural factors can also add to the optical signals and complicate the physiological interpretation of remotely sensed data. We wanted to know to what extent canopy structure and ground vegetation affect the fluorescence signal as measured over a canopy. For this purpose we modified a 3D radiative transfer model (DART) to accommodate different canopy layers as well as a vegetated background (See abstract by Weiwei et al). This model will be next used to quantitatively interpret spatial variations in SIF acquired with a drone flying over a complex forest canopy.

4. BIOGEOCHEMICAL CYCLES, SOIL PROCESSES AND ELEMENT BUDGETS

Biogeochemistry concerns cycling of elements in terrestrial as well as aquatic ecosystems by integrating physics, chemistry, geology and biology. Besides natural ecosystems, it also deals with systems altered by human activity such as forests under different management regimes, drained peatlands and lakes loaded by excess nutrients. The most important elements under study are carbon, nitrogen and phosphorus, which are vital for ecosystem functioning and processes such as photosynthesis, i.e. uptake of inorganic carbon by plants. Biogeochemistry focuses on interphases of scientific disciplines and by doing so, it also combines different research methods. We treat the ecosystems as open entities which are closely connected to atmosphere and where water is among the key transport mechanisms.

Disturbances and biogeochemistry (Köster, Pumpanen & Berninger et al)

The work under research theme “disturbances and biogeochemistry” is currently focusing on the effects of disturbances (fire, reindeer grazing) on the biogeochemical cycles in boreal and sub-arctic forests, and the effect of charcoal (industrially produced biochar) on the C and N dynamics in boreal forests.

Our study from northern boreal fire chronosequence (Yukon, Canada) showed that soils were warmer and drier, and soil C content was lower on recently burned areas. The depth of the active layer on top of permafrost was increasing rapidly after the fire. Thus, the time passed from last forest fire has a long lasting impact upon many experimental factors (Köster et al., 2017). The thawing of near-surface permafrost directly affected the GHG fluxes (Köster et al., 2017). Soil CO₂ efflux decreased shortly after the fire, but increased then rapidly. Subarctic boreal forests acted as sinks of CH₄ in our study, but changes in CH₄ fluxes lasted for a short period of time. A slight decrease in N₂O emission could be observed in comparison of different fire age classes.

Our study dealing with reindeer grazing in northern boreal forests (Värriö Strict Nature Reserve, Finnish Lapland) showed that grazing by reindeer significantly affected lichen and moss biomasses in these forests. Our results indicated that grazing by reindeer in the northern boreal forests affects the GHG emissions from the forest floor and these emissions largely depend on changes in vegetation composition. Soil was always found to be a source of CO₂, and soil CO₂ emissions were significantly
smaller in non-grazed (Köster et al., 2017b). The soils in our study areas were CH$_4$ sinks through entire measurement period, and grazed areas consumed more CH$_4$ compared to non-grazed areas (Köster et al., 2017b). We also observed that the N$_2$O emissions were significantly affected by moss biomass and soil temperature. Non-grazed areas with lower moss biomass and soil temperature were a small sink of N$_2$O while the total fluxes remained around zero in the grazed areas (Köster et al., 2017b).

Our study dealing with the addition of biochar to forest soil (Hyytiälä, Finland) showed that added biochar (with different treatments) had no significant effect on soil microbial biomass, the rates of N mineralization, nitrification and biological N fixation (Palviainen et al., 2017). The results suggest that wood biochar additions of 5–10 t ha$^{-1}$ to boreal forest soil does not cause strong effects and threat to the native soil C stocks because increase in soil CO$_2$ effluxes were rather small and vanished during the second year after biochar amendment (Palviainen et al., 2017). Thus, it seems that biochar is a promising tool to sequester C into the soil in boreal forests.

**Soil processes (Heinonsalo et al)**

The research team of doc. Jussi Heinonsalo has the aim to investigate how plant’s belowground carbon (C) allocation affects soil organic matter (SOM) decomposition and its atmospheric feedbacks. The backbone of the group has been the Academy research fellow project NITROFUNGI that ended 31.8.2017.

Plants were shown to cause drastic, direct changes in SOM decomposition. Significant mass loss of SOM was observed in the greenhouse incubations if Scots pine tree seedling was present, compared to non-planted soil treatments (Kieloaho et al. 2016). The mechanism behind increased SOM mass loss seems to be enzymatic, suggesting plant’s stimulation of root-associated microbes and their SOM degradation-related enzyme excretion. In another study, understory dwarf shrubs species (*Calluna vulgaris*, *Vaccinium myrtillus* and *V. vitis-idaea*) were shown to alter SOM chemistry differently than Scots pine, mainly due to decrease in pH and increase in condensed tannin content in soil (Adamczyk et al. 2016). Fungal necromass, that is very abundant source of nitrogen (N)-rich organic matter in forest soils, was shown to form complexes with condensed tannins resulting in its decreased decomposability. This recent finding pinpoints a novel mechanism that would partly explain surprisingly slow decomposition rate of microbial litter (Adamczyk et al. manuscript). In a fourth study, a field experiment, plant-derived C flow was restricted to form three different treatments where either no C from host plant, C only through mycorrhizal fungal hyphae or non-limited C flow were allowed. Similar observation was made as in the greenhouse studies: soil pH got lower and SOM mass loss higher the more plant-derived C accessed SOM. Also, the more recalcitrant forms of N were abundant if the plant C flow was unrestricted (Adamczyk et al. manuscript). These result suggest that rather than a passive role as producer of litter, plants have a dynamic impact in SOM decomposition and formation, which is necessary to take into account in soil and ecosystem carbon modelling.

From microbial perspective, soil fungal community structure at SMEARII station was thoroughly investigated using latest NGS sequencing methods. Fungal community structure was shown to be species-rich and diverse also in deeper mineral soil horizons. Seasonally the community remained rather stable during growing season but drastic changes seem to occur between summer and winter seasons (Santalahti et al. 2016). As fungal biomass was shown to be a large reservoir of amines, the community shift may cause release of fungal cell content (like amines) that are linked to atmospheric emissions (Kieloaho et al. 2016). Understory dwarf shrub plants were also shown to host different fungal and bacterial communities (Timonen et al. 2016, Sietiö et al manuscript) with potential feedbacks to GHG emissions (Halmeenmäki et al. 2017).

Soil chemical and microbial processes were also investigated in the field with respect to their feedback to CO$_2$ or other GHG emissions. Plant-derived C flow to soil was shown not to affect significantly soil BVOC emissions (Mäki et al. 2016) or methane emission (Pihlatie et al. manuscript) but additional C flow to soil causes significant rhizosphere priming effect (RPE), i.e. increased heterotrophic respiration (Heinonsalo et al. manuscript). Tree-root exclusion experiment also gave novel information on soil CO$_2$ sources (Ryhti et al. manuscript) and separation of autotrophic and heterotrophic soil respiration
(Pumpanen et al. manuscript). Ground vegetation ericoid plant species were also shown to differ significantly from trees in terms of their C dynamics, having potential implications to interpretations of the sources of CO₂, measured with standard manual soil chambers in most field stations (Kulmala et al. 2017).

Four years of CO₂ exchange measurements reveal that the ecosystem scale fluxes are strongly temperature-limited in a subarctic Scots pine stand, SMEAR I (Kulmala L. et al)

The ground layer in sub-arctic forests is colonized by a dense community of plant species consisting mainly of ericaceous shrubs, mosses and lichens. These are photosynthetically very active since the canopy coverage is rather sparse and there is plenty of light available in comparison with the forest floor in boreal forests. We aimed to explore the CO₂ exchange dynamics in a such open stand and to come up with a more reliable estimate on how trees and the forest carbon sink in such forests might behave in the future. Thus, we measured CO₂ fluxes with Eddy Covariance (EC) technique in a subarctic Scots pine (Pinus sylvestris L.) stand, SMEARI, in 2012–2015. In addition, we combined the automatic chamber measurements of pine shoot CO₂ exchange, the optimum stomatal control model and a stand photosynthesis program to model the photosynthesis of the tree canopy only. Instead of upscaling the shoot chamber measurements as such, the model included also tree characteristics and light attenuation in the canopy. Then, the photosynthesis of ground vegetation was determined as the difference between the EC-derived ecosystem scale photosynthesis and the modelled canopy photosynthesis. We found that canopy photosynthesis increased already in April whereas that of ground vegetation started to increase only after snow melt in mid-May. Their rate of photosynthesis roughly equalled after midsummer and decreased more or less with same manner in the autumn with decreasing temperatures and light intensity. The results highlight that the spring recovery of ecosystem scale photosynthesis cannot be modelled using only the history of air temperature as an input but the timing of snowmelt must be also considered in such open forests where ground vegetation has a notable share in the primary product.

Soil phosphorus concentration determines ground vegetation dynamics in a subarctic forest ecosystem (Matkala et al)

Though nitrogen is often limiting growth in boreal forests, also phosphorus may have an important role in these ecosystems. We had research sites around Sokli region in Eastern Lapland. Part of the sites were located on phosphorus rich soils, which gave us the possibility to do comparisons between different levels of soil phosphorus. Although our statistical modelling processes are still in progress, we can tell that there are connections both with needle total phosphorus concentration and soil total phosphorus concentration. In a similar way, ground vegetation and soil total phosphorus seem to be connected so that ground vegetation has a bigger number of forbs and graminoids when soil total phosphorus is high compared to sites where it is lower.

Revealing the sources of methane and nitrous oxide in boreal forests (Pihlatie et al.)

Boreal upland forests are traditionally considered as a globally important methane (CH₄) sink and a small source of nitrous oxide (N₂O) due to microbial C and N turnover processes in the soil. There is an increasing evidence that vegetation can act as a source of both greenhouse gases, while the production mechanisms in plants and their contribution to the ecosystem CH₄ and N₂O exchange are yet largely unspecified. We have conducted a series of laboratory and field experiments to evaluate the capacity of boreal trees to exchange CH₄ and N₂O and to understand their role in the CH₄ and N₂O balances of boreal forests. The field experiments have been conducted at two sites in southern Finland: a drained peatland forest in Lettosuo, and an upland forest in Hyrylä.

We found that the forest floor at both sites acted as a sink of CH₄, while the exchange of N₂O varied between a significant source in Lettosuo to a small sink in Hyrylä. The emissions from trees significantly contributed to the net CH₄ and N₂O emissions from boreal forests. Tree stems emitted small amounts of CH₄ and N₂O throughout the year, with the highest emission rates occurring during the summer from trees growing on wet locations. Tree species and growth conditions affected differently to CH₄ and N₂O emission rates from tree stems suggesting towards different transport pathways of CH₄ and N₂O.
N₂O from the soil to the atmosphere. The results from Hyytiälä upland forest also indicate that tree canopies dominate the whole-tree emissions of both CH₄ and N₂O, demonstrating the need for more studies focusing on leaf-level CH₄ and N₂O exchange in forest ecosystems.

The microbial analysis support our hypothesis that methanogens are involved in the CH₄ production in the soil, while they may not significantly contribute to the in situ CH₄ production within trees or aboveground vegetation. Furthermore, it seems that not only soil but also vegetation plays a role in the CH₄ consumption. The role of microbes in N₂O exchange of trees remains to be evaluated, however, our results confirm that different forest compartments contribute to the net CH₄ and N₂O exchange of boreal forest ecosystems through the microbes, tree physiology and possibly via abiotic processes.

5. FOREST MODELLING

Methods for regional-scale monitoring and predicting forest carbon fluxes and stocks (Mäkelä et al)

The objective of this work is to develop methods that allow us to make large-scale predictions of the development of forest stocks and fluxes as influenced by climate and forest management. We have developed a model system consisting of a climate-driven model (PRELES) of gross primary production (GPP) and linked this with a forest growth model (CROBAS) that can be run using either ground-based or satellite observations to initialise the model. Work has been carried out to calibrate these models using Bayesian calibration (PRELES for boreal sites: Minunno et al. 2016, PRELES for temperate and subtropical sites: Tian et al. in prep, CROBAS for boreal sites: Minunno et al. in prep) and to analyse their prediction uncertainties in relation to climate model, climate scenarios, uncertainty about impact processes and model parameter uncertainty (Kalliokoski et al. in prep). The models are also being linked with the soil carbon model Yasso for the regional estimation of NEE. The model system has been linked to EO data provided by VTT, which includes novel EO data analysis results of forest variables needed for initialising the models (Mäkelä et al. in prep). Our estimates of the current growth of the growing stock in Finland are well in line with forest statistics, and our GPP results agree with flux tower measurements. The model system has also been linked to the multisource inventory data available with Luke (Härkönen et al. in prep), and scenario results with climate scenarios have been input the Climate Guide web site maintained by FMI.

Model development to incorporate old-growth and uneven-aged stands (Mäkelä et al)

This work aims at improving our growth models to be readily applicable to continuous cover management and old-growth stands which both have been suggested to contribute to climate change mitigation by means of increasing the total carbon sequestration of forests (Kalliokoski et al. 2016, Mäkelä et al. 2016). Empirical studies to support both objectives are underway (Kumpu et al. in prep, Liu et al. in prep).

Within-season growth and phenology (Mäkelä et al)

The objective of this work is to increase our understanding of the within-season timing of carbon acquisition and allocation to growth of the different plant components, in order to be able to analyse and predict the impacts of climate change on growth. A whole-tree model has been developed earlier (Schiestl-Aalto et al. 2015) where temperature is the key environmental control (Schiestl-Aalto and Mäkelä 2017).

Newtonian boreal forest ecology: The Scots pine ecosystem as an example (Hari et al)

Isaac Newton's approach to developing theories in his book Principia Mathematica proceeds in four steps. First, he defines various concepts, second, he formulates axioms utilising the concepts, third, he mathematically analyses the behaviour of the system defined by the concepts and axioms obtaining predictions and fourth, he tests the predictions with measurements. In Hari et al (2017a), we formulated our theory of boreal forest ecosystems, called NewtonForest, following the four steps introduced by Newton. The forest ecosystem is a complicated entity and hence we needed altogether 27 concepts to
describe the material and energy flows in the metabolism of trees, ground vegetation and microbes in the soil, and to describe the regularities in tree structure. Thereafter we formulated 34 axioms describing the most important features in the behaviour of the forest ecosystem. We utilised numerical simulations in the analysis of the behaviour of the system resulting in clear predictions that could be tested with field data. We collected retrospective time series of diameters and heights for test material from 6 stands in southern Finland and five stands in Estonia. The numerical simulations succeeded to predict the measured diameters and heights, providing clear corroboration with our theory.

We continued the analysis utilizing data from SMEAR I, to connect theoretically the fundamental concepts affecting C3 photosynthesis with the main environmental drivers (ambient temperature and solar light intensity (Hari et al 2017 b, c). The light and carbon reactions in photosynthesis are based on the coherent operation of the photosynthetic machinery, which is formed of a complicated chain of enzymes, membrane pumps and pigments. A powerful biochemical regulation system has emerged in evolution to match photosynthesis with the annual cycle in solar light and temperature. The action of the biochemical regulation system generates the annual cycle of photosynthesis and emergent properties, the state of photosynthetic machinery, and the efficiency of photosynthesis. The state and the efficiency of the photosynthetic machinery is dynamically changing due to biosynthesis and decomposition of the molecules. The mathematical analysis of the system resulted in exact predictions of the behaviour of daily and annual patterns in photosynthesis. We tested the predictions with extensive field measurements of Scots pine photosynthesis in Northern Finland and four other sites from north to central Europe. Our theory gained strong corroboration for the theory in the rigorous tests, and has strong implications on the interpretation of the effects of the global change on the processes in boreal forests, especially of the changes in the metabolic annual cycle of photosynthesis.

6. **SOCIETAL IMPACT**

**Sustainability and multi-functionality of European forests (Bäck et al)**

The interaction of forests with climate change is complex. The function given the highest priority in the 2015 Paris Agreement of the UNFCCC is to manage forests sustainably so as to enhance forest carbon stocks in order to help mitigate climate change. EU forests are already contributing to this through their annual increment of wood, which is currently equivalent to an uptake of about 100 million tonnes of carbon annually (approx. 10% of Europe's fossil fuel emissions). However, science suggests that the processes underlying this may be transient and that the forest-based carbon sink has an upper limit, which may already have been reached in some areas. Nevertheless, potential may still exist for increasing the carbon sink of European forests through well-designed management. Here, while younger, faster growing forests may have a higher rate of carbon uptake from the atmosphere, it is the older longer-rotation forests and protected old growth forests which exhibit the highest carbon stocks.

The overall impacts of forests on the atmospheric carbon budget depend heavily on the uses made of the harvested forest products (wood). Where the wood is captured in construction or other long-term uses, its carbon is kept out of the atmosphere for long periods and the demand for other carbon-intensive materials such as steel or concrete is reduced. In contrast, the use of wood in bioenergy releases its carbon to the atmosphere very swiftly. In assessing overall climate impacts therefore, the whole chain from forest ecosystem to wood products and energy substitution needs to be taken into account. In addition, forests influence climate by biophysical processes, such as cloud formation processes and albedo, which depend on tree species diversity, stand density, types of forest management, and location. Depending on the combination of the above factors, the impacts of forests on global average temperatures can be positive or negative. This report examines aspects related to the net effect of forests on climate, including the net effects on climate of using forest biomass as a source of fuel and its comparison with fossil fuels.

The EASAC (2017) report examines the need to recognize the multiple uses and the importance of different ecosystem services (ES) provided by Europe’s forests. The report points out that the principles of Sustainable Forest Management (SFM) applied in the EU recognize the multi-functionality of forests.
and the need to maintain the ecological functions of forests and their ecosystem services, while fulfilling their economic and social functions. However, Europe’s forest ecosystems are under pressure due to existing impacts of climate change and forest management, and are expected to become more stressed in the future. In addition to climate change, human efforts to mitigate and adapt to climate change can both positively and negatively affect biodiversity and other ecosystem services. Our analyses thus shows tensions between some of the objectives of SFM – especially between demands for increased extraction of biomass from forests and the contributions made by the same biomass in situ to soil fertility, biodiversity and protective functions. Other synergies and trade-offs exist in the way in which forests’ interaction with climate change mitigation is managed (see also Vesala & Bäck this issue).

Overall, the current scientific evidence on forests’ role in climate change and on the current status of both biodiversity and forest vitality has significant implications for future forest policies and management. Policies should better account for the multi-functionality of forests and should better optimize the balance between social, economic and ecological contributions. To find a better balance between the competing demands on Europe’s forests may require different management approaches. For instance, depending on location, forest management strategies such as continuous cover silviculture and the enhancement of native tree species diversity and of landscape heterogeneity may simultaneously contribute to the maintenance of forest cover, the conservation of carbon stocks and biodiversity, whilst improving the social and cultural values of forests.

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VOC GROUP ACTIVITIES

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Keywords: hydroxyl radical (OH), OH reactivity, biogenic volatile organic compounds (BVOCs)

INTRODUCTION

Many plants have distinctive smells made of chemical compounds which they use to communicate. They can either attract pollinators, repel herbivores or respond to other stress factors by releasing massive amounts of volatile organic compounds (VOCs) to the air. Globally, these biogenic emissions are estimated to reach 760 Tg C yr⁻¹ and chemically they mainly consist of isoprene (ISO), monoterpenes (MT), sesquiterpenes (SQT), methanol and acetone (Sindelarova et al., 2014). The terrestrial biogenic VOCs account for about 90% of the emission total (Guenther et al., 1997). Most of the emitted compounds have high reactivity in the atmosphere and their lifetimes vary from minutes to hours. This means that they strongly affect the oxidative capacity of the atmosphere both locally and regionally. When oxidised they form less volatile compounds, which eventually contribute to secondary organic aerosol thus also affecting Earth’s radiative budget.

During the last couple of decades the concept of atmospheric hydroxyl radical (OH) reactivity has been introduced to describe the VOC content of the air. By measuring how much OH radicals are consumed in the reactions and comparing this amount with the measurements of everything we know that reacts in the air with OH radicals, we can evaluate how much unknown reactive compounds are present in the atmosphere. Several studies have shown that this gap is large, for example in boreal forest from 50 to 85% (Sinha et al., 2010; Nölscher et al., 2013). Therefore, we need to search for new compounds and sources responsible for atmospheric reactivity. New measurement techniques such as proton transfer reaction time of flight (PTR-TOF) mass spectrometers enable fast response measurements of several VOCs and identification of new compounds and sources.

METHODS

The OH reactivity has been measured in Hyytiälä using the Comparative Reactivity Method (CRM, see Sinha et al., 2008). The method is also described in the abstract by Praplan et al. (this issue) and with more detail in Praplan et al., 2017.

In addition to total OH reactivity measurements reactive organic compounds were also measured with two in situ GC-MS (for C₆-C₁₀ hydrocarbons and oxygenated VOCs). These methods are described in Hellén et al. (this issue). Additional sampling took place on two occasions in canisters for light hydrocarbons (C₂-C₆ hydrocarbons) and carbonyls. The reactivity \( R_{OH} \) derived from the sum of individual compounds \( X_i \) combined to their respective reaction rate coefficient with OH \( (k_{OH+X_i}) \) is calculated according to the following equation.

\[
R_{OH} = \sum_i k_{OH+X_i}[X_i]
\]
Our analysis includes over 100 individual species from two GC-MS, GC-FID and LC-UV measurements. In addition nitrogen oxides, ozone, sulfur dioxide, and carbon monoxide were retrieved from the mast of the SMEAR II station, about 80 m away from the sampling position of total OH reactivity and VOCs.

New BVOC sources have been surged; Mäki et al. (this issue) have measured BVOCs in soil air space and their fluxes to the atmosphere while Vanhatalo et al. (this issue) have measured BVOCs emitted by tree stems. The methods are described in their abstracts.

RESULTS AND DISCUSSION

Our reactivity measurements are unique since they cover a longer time than typical measurement campaigns for OH reactivity. The preliminary experimental total OH reactivity values measured ($R_{expt}$) are displayed in Figure 1. The average reactivity measured between 15 April and 30 July is $12.4 \pm 8.9$ s$^{-1}$. This average is slightly higher than previous studies in summer at the same site (Sinha et al., 2010; Nölscher et al., 2012). Higher reactivity values were usually found at night, following the BVOCs concentrations pattern, except for high afternoon values observed during the week after soil temperature rose the first time above 1.5°C that year. The over 100 compounds quantified do not add up to the experimental reactivity measured.

Figure 2 shows the mean concentrations of different VOCs at 20°C. Due to high reactivity of SQTs, their ambient mixing ratios are quite low even if the emissions are relatively high. Of the SQTs β-caryophyllene had highest mixing ratios, but in summer also longicyclene, β-farnesene and 4 unidentified SQTs were detected. Temperature seemed to be the most important factor explaining seasonal and daily variations of BVOC concentrations, monthly and daily means of MTs and SQTs had very strong correlation with temperature (Hellén et al., this issue).

Soil seems to be an important source of terpenoid compounds, especially SQT fluxes have been found to be significant in a study by Mäki et al. (Fig. 3). Over 50 VOCs were found from the air space in the boreal soil and especially organic soil was found to be a significant isoprenoid source (Mäki et al., this issue). Relatively high isoprenoid concentrations were also measured under snow cover, as snow and ice cover hinders gas diffusion and causes belowground accumulation of VOCs. Understorey vegetation was found to be a monoterpene sink and VOC fluxes from boreal forest floor were regulated by vegetation sink effect, temperature and seasonality, mainly litterfall production of needles in fall (Mäki et al., 2017).

Until recently there has been an almost total lack of information about the BVOC emissions from woody parts of living trees. Vanhatalo et al. (this issue) measured the vertical variation of emissions in the tree stem and found measurable emissions of monoterpenes and methanol from Scots pine stems in situ. The upper part of the stem dominated the monoterpene emissions from Scots pine. Considering that the foliage is located in the uppermost part of the tree as well, it is reasonable to say that the clear majority of Scots pine monoterpene emissions are released into the ambient forest air at the canopy heights.

The new mass-spectrometers enable fast response measurements of VOCs and also small oxygen containing compounds such as methanol, acetone and acetaldehyde that are challenging for gas-chromatographs. Proton transfer reaction time of flight (PTR-TOF) mass spectrometer has been used for measurements of VOCs in Hyytiälä and in Bosco Fontana, Italy. The method is described in Schallhart et al., 2016 and 2017. The measurements in this work resulted in the quantification of the total exchange in a broadleaf forest in Bosco Fontana, Italy, and a conifer forest in Hyytiälä, Finland. By using a new automated method, 29 VOCs with exchange were measured in Bosco Fontana and 25 VOCs in Hyytiälä. These two ecosystems differ as the major terpene emissions are isoprene for the oak forest and monoterpenes for the scots pine forest as shown in Figs. 4 and 5.
Figure 1. Preliminary experimental total OH reactivity ($R_{exp}$) with 1-h averages, and 1-h averages of OH reactivity calculated from individually measured compounds ($R_{OH}$).

Figure 2. Mean mixing ratios of different BVOCs scaled to 20°C and exponential correlation ($R^2$) of daily mean mixing ratios with temperature measured at SMEAR II in Jun-Aug 2016.
Figure 3. The total isoprene, MT, and SQT flux (μg m$^{-2}$ h$^{-1}$) from forest floor from April to December in 2016.

Figure 4: PTR-ToFMS fluxes from a boreal forest, SMEAR II

Figure 5: PTR-ToFMS fluxes from an oak forest, Bosco Fontana, Italy.
FUTURE PLANS

We have compared the total OH reactivity $R_{OH}$ derived from measurements of over 100 individual compounds to the experimental total OH reactivity $R_{exp}$ measured at the boreal forest station SMEARII during a period covering over two months. $R_{exp}$ turned out to be much higher than $R_{OH}$ for most of the measurement period. The missing compounds might be different types of VOCs that were not measured and are difficult to sample and analyse in situ and off-line due to their high reactivities.

To detect also the fastest reacting compounds, we have already measured reactivities together with BVOC content directly from emission instead of ambient air. The measurements are still on-going. Our future plan is to cover also less volatile compounds, such as diterpenes, that could potentially have important addition to the reactivities. Matsunaga et al. (2011) have measured the emissions of a diterpene, kaur-16-ene, from typical Japanese conifers, showing that these emissions are of the same magnitude as those of monoterpenes. These results suggest that diterpenes could contribute significantly to the missing OH reactivity in boreal forests.

We will also develop a new method for ozone reactivity measurements. Ozone reacts with compounds with double carbon bonds, such as monoterpenes, sesquiterpenes, and diterpenes and some of their oxidation products, thus further assisting the understanding of the missing sink for OH in boreal forest air.

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SUMMARY ON THE ACTIVITIES OF THE AEROSOLS AND IONS GROUP DURING YEAR 2016-2017

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Keywords: aerosol particles, atmosphere, instrumentation, nucleation

INTRODUCTION

Aerosols and ions group (AIGG) is a measurement oriented research group at the University of Helsinki, Department of Physics, Division of Atmospheric Sciences. AIGG performs laboratory experiments spanning from cluster synthesis to cloud droplet activation and field measurements in various environments from boreal forest in Hyytiälä to Amazonian rainforest, and is also active in instrument development. The aims of AIGG are to provide reliable observations of the physical properties of aerosol particles and gain new understanding of processes related to new particle formation (NPF), particle growth and cloud droplet formation. The following abstract presents the latest progress of AIGG in atmospheric measurements, chamber studies and laboratory experiments, together with a brief outlook into the future.

ATMOSPHERIC MEASUREMENTS

During 2016-2017 AIGG has contributed to long-term field measurements at the SMEAR station network and participated to intensive campaigns in Greenland Station Nord, Svalbard Ålesund, Pallas Finland, Granada Spain and organized a spring campaign at SMEAR II in Hyytiälä with flight measurements using Cessna aircraft and drones from FMI and aerosol particle flux measurements. During August 2017 we started long-term observations of cluster and nano-particles using AIS and PSM at SMEAR I station in Väriö. The activities in northern Finland also included flight measurements with Cessna and PSM measurements at Pallas. AIGG also contributes to the building of a second SMEAR station in urban Beijing area.

Several publications came out reporting atmospheric observations of clusters and new particle formation: Jokinen et al. (2017) demonstrate the importance of photochemistry in NPF using long-term continuous measurements at boreal forest site Hyytiälä. The production of gaseous particle precursors stops due to lack of sunlight during a solar eclipse, which also immediately impacts the formation of particles.

Dada et al. (2017) studied new particle formation events in Hyytiälä, but only considered clear-sky conditions in the statistical analysis to exclude the impact of different weather conditions. The main finding of the study was that condensation sink and temperature are the main variables separating event and non-event days during springtime.

Kontkanen et al. (2017) collected the first global data set of sub-3 nm size distribution measurements using the PSM. Their main conclusions are that the sub-3 nm particle concentrations are mostly determined by the availability of the precursor vapors, which leads to higher sub-3 nm particle concentrations during daytime compared to night-time at all measurement sites, while condensation sink seemed not to limit the formation of clusters.

Sipilä et al. (2016) show how particles nucleate rapidly at the coast of Atlantic ocean, Ireland, from iodine oxoacids without involvement of sulphuric acid. It is the first time that atmospheric nucleation has been resolved on a molecular level.
Wimmer et al. (2017) report direct observations of small ions and nucleation mode particles in Amazonas. Comparing measurements at two sites near Manaus in Brazil, they conclude that nucleation events happen on an open pasture site during wet season, but not during dry season and nor at the site inside rainforest canopy.

LABORATORY EXPERIMENTS

AIGG has been involved in several different laboratory studies and published several papers during 2016-2017:

In collaboration with Beneq Ltd, Ahonen et al. (2017) report intensive particle production in cleanroom environments, where ALD (atomic layer deposition) techniques are used. ALD instrument maintenance releases a significant amount of precursor vapors, which, in the absence of condensation sink, turn rapidly into particles.

Steiner et al. (2017) studied sub-3 nm charged cluster-cluster recombination using new technique: two high resolution DMAs operated at opposite polarities, from which the ions are guided into a recombination cell. Recombination products were measured with the PSM and modelled using simple collision based model.

Fang et al. (2017); Wang et al. (2017a); Wang et al. (2017b) report a series of experiments conducted in the Helsinki aerosol laboratory using a combination of flame reactor-high resolution DMA-PSM-mass spectrometer instrumentation. Their major findings include for example unexpectedly high ion fractions in tetraethyl orthosilicate and titanium isopropoxide doped flames, measured incipient stable cluster densities and chemical compositions, and chemical pathways leading to cluster and particle formation in doped flames.

The involvement of AIGG in the CLOUD experiment at CERN remains strong. Wagner et al. (2017) used a new nano-particle counter set-up to study ion-induced nucleation in different chemical systems in the CLOUD chamber. Several other important CLOUD papers were published: Kürten et al. (2016) summarizes the experimental nucleation rates from sulphuric acid under different ammonia concentrations, temperatures and ionization rates. Dunne et al. used these results in a global aerosol model to estimate the significance of the particle formation mechanisms studied at CLOUD on a global scale. Gordon et al. 2016 and 2017 included pure biogenic nucleation mechanism in the global aerosol model and studied its impact in present day and pre-industrial atmospheres.

INSTRUMENT DEVELOPMENT

During 2016-2017 AIGG organized a prototype CPC (Condensation Particle Counter) workshop at Helsinki aerosol laboratory, began developing a new high flow ultrafine CPC, a light-weight CPC and an optimized sub-10 nm particle size distribution measurement instrument. The high flow ultrafine CPC is currently operated in Hyytiälä on a long-term basis, while the sub-10 nm particle sizer was deployed in Hyytiälä during a field campaign.

Kangasluoma et al. (2017) report characterization of three new sub-3 nm CPCs during Helsinki prototype CPC workshop. The characterized CPCs were: TSI nano enhancer, ADI versatile water CPC and homemade 3010 type CPC from University Blaise Pascal.

Kangasluoma and Kontkanen (2017) studied the uncertainties related to the sub-3 nm particle concentration measurements. Their main findings are that the largest sources of uncertainty in the particle concentration measurement are uncertainties in the CPC lowest detectable diameter and steep particle size distributions as a function of particle size. Additionally they studied how low counting statistics can affect the measured particle concentrations.
The group was also involved in the study of Pinterich et al. (2016), who reports the development of Size Analyzing Nucleus Counter (vSANC) at the University of Vienna, and its first employment for field measurements at Hyytiälä.

CONCLUSIONS AND FUTURE OUTLOOK

The previous year was productive for the AIGG in terms of experiments and publications. Still on-going analysis is related e.g. to a successful campaign in Siikaneva peatland site, understanding the connection of roll vortices to NFP in the boundary layer, so called “Hyytiälä simulation” experiment in the CLOUD chamber, and work toward optical closure of particle properties. Future efforts include new experiments in the CLOUD chamber and field measurement campaigns at a mountain site at Chacaltaya Bolivia and Marambio Antarctica. Several new instrument development projects were started and continued from the previous year concentrating on the sub 10 nm particle sizing and fast counting, and efforts for starting drone based measurements are put forward.

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AN OVERVIEW OF THE ACTIVITIES BY AEROSOL-CLOUD-CLIMATE INTERACTIONS GROUP OF THE UNIVERSITY OF HELSINKI


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INTRODUCTION

Concentrations of greenhouse gases, aerosol particles and reactive trace gases are tightly connected with each other via physical, chemical and biological processes occurring in the atmosphere, biosphere and at their interface (Arnth et al. 2010, Carslaw et al. 2010, Paasonen et al. 2013, Stocker et al. 2013, Unger 2014, Andrea et al. 2015, Tian et al. 2016, Green et al. 2017). About a decade ago Kulmala et al. (2004) suggested a negative climate feedback mechanism whereby higher temperatures and CO2-levels boost continental biomass production and volatile organic compound (VOC) emissions, leading to increased biogenic secondary organic aerosol (SOA) and cloud condensation nuclei (CCN) concentrations, and by that way tending to cause cooling in a manner similar to the CLAW-hypothesis that linked climate change with the ocean biochemistry (Charlson et al. 1987, Quinn and Bates 2011). Kulmala et al. (2013, 2014) extended the idea of the continental biosphere-aerosol-cloud-climate (COBACC) feedback further by adding the connection between aerosol particles, radiation and gross primary production (GPP) which is a measure of ecosystem-scale photosynthesis. In this extended view, the COBACC feedback mechanism has two major overlapping feedback loops, both initiated by increased CO2 concentrations and acting toward suppressing global warming (Fig. 1).

Figure 1. The feedback loops associated with the COBACC feedback (Kulmala et al., 2013, 2014). Here GPP is gross-primary production, BVOC and SOA refer to biogenic volatile organic compounds and secondary organic aerosol, respectively, CS is the condensation sink, \( A_{\text{tot}} \) and \( V_{\text{tot}} \) are the total aerosol surface area and volume concentrations, respectively, CCN refers to cloud condensation nuclei, and CDNC is the cloud droplet number concentration.

Most of the work made within the aerosol-cloud-climate interactions group can be tied to the lower branch of the COBACC feedback mechanism that connects biogenic VOC emissions, atmospheric new-particle
formation and growth, CCN formation, interaction of aerosols with clouds, indirect radiative effects, and the ambient temperature. Below we will summarize the current status of this work.

ADVANCES IN UNDERSTANDING AND HIGHLIGHTS OF THE RESULTS

Emission of biogenic VOCs and their influence on new particle formation

Trees emit a variety of VOCs, but the source strength and spectra of the emitted VOCs depend on physical, environmental and biological conditions. Taipale et al (Abstract in this collection) constructed a new model to investigate the impact of biotic plant stress on new particle formation (NPF) and growth. They found that the occurrence and intensity of NPF depend highly on the specific stressor: gypsy-moth infected oak can produce more new particles than what has been observed by non-stressed boreal forest. Autumnal moth-infected birch does not lead to NPF, and due to the isoprene/monoterpene ratio, it is unsure whether the investigated fungal infections lead to NPF.

Atmospheric new particle formation and growth

In this subject area, we have been involved in field observations and related theoretical studies. Kontkanen et al. (2017) compared concentrations of sub-3 nm atmospheric particles measured with a Particle Size Magnifier at nine locations around the world. Sub-3 nm particle concentrations were observed to be highest at the sites with strong anthropogenic influence. In boreal forest, sub-3 nm particle concentrations were higher in summer than in winter, indicating the importance of biogenic precursor vapors. At all the study sites, particle concentrations were higher during daytime than at night. When comparing the total sub-3 nm particle concentrations to ion concentrations, electrically neutral particles were found to dominate in polluted environments and in boreal forest during spring and summer.

Dada et al. (2017) combined 20 years of observations of atmospheric NPF at the SMEAR II station in Finland. The analysis revealed that, as one would expect, the frequency of NPF events is higher under clear-sky conditions compared with cloudy conditions. By focusing on clear-sky conditions, notable differences in many variables were observed between the NPF event and non-event days. For spring time, a threshold value for the ambient temperature and condensation sink (CS) combined was found, above which practically no NPF events could be observed. In another study, Dada et al. (abstract in this collection) investigated the impacts of different organic vapors and NO\textsubscript{x} on new particle formation and growth rates in the CLOUD chamber at CERN. They varied the atmospherically relevant concentrations of monoterpenes, sesquiterpene, isoprene and NO\textsubscript{x}, and studied the resulting aerosol formation rates and size spectra of the Highly Oxidized Molecules (HOMs).

Using Air Ion Spectrometer measurements, Chen et al. (2017) observed NPF on 85 days out of 330 measurements days on the Antarctic Plateau (3220 m above the sea level). Most of the NPF events took place during summer time, and the days with NPF tended to have higher cluster ion concentrations and condensation sink compared with days with no NPF events. Newly-formed particles grew in size up to a few tens of nm with typical growth rates of a few nm/hour.

Hakala et al. (abstract in this collection) analyzed NPF at rural background site in Western Saudi-Arabia. They showed that NPF events occur very frequently, during 70 – 95 % of all the days. These NPF events are strong both in terms of new particle formation rate and particle growth rate. In most cases the observed particle modes showed a decrease in the mode mean diameter towards the end of the event. Based on trajectory analysis, the NPF events initiated at the coastal areas, where strong anthropogenic sulfur emissions take place. During the easterly winds from inlands, NPF events were typically not observed.
Zaidan et al. (abstract in this collection) produced a machine learning-based Bayesian neural network for automatic classification of NPF event and non-event days. This automatic classifier managed to classify close to 85% of days at the SMEAR II station similarly than the traditional visual-based method (Dal Maso et al., 2005).

Growth rates (GR) of newly-formed particles have been reported mainly for the nucleation mode, and extremely rarely for particle sizes relevant for cloud condensation nuclei (CCN). Peltola et al. (abstract in this collection) used a new automatic method for particle number size distribution data measured at the SMEAR II station in Finland, and determined GR for a wide range of particle sizes (a few nm up to about 200 nm in particle diameter). The analysis showed that GR tends to increase with an increasing particle size, not only for the nucleation mode and observed in many earlier studies, but all the way up to particle diameters >100 nm. This finding has important implications on our understanding of mechanisms responsible for growing newly-formed particles, and ultimately their influence of atmospheric CCN.

Based on our current theoretical understanding, atmospheric NPF should not occur at very high aerosol loadings because of the large sink that pre-existing aerosol particles cause for molecular clusters and growing nanoparticles. Kulmala et al. (2017) investigated potential explanations for the observations that NPF does take place under extremely polluted conditions encountered in Chinese megacities. They found that NPF is possible under such condition only if molecular clusters are scavenged considerably less efficiently than one would expect based on their collision rates with pre-existing particles, or if they grow much faster in size than our current understanding allows.

Condensation sink (CS) is one of the most important variables in analyzing atmospheric NPF and its connection with vapor condensation and particle growth. Ezhova et al. (Abstract in this collection) derived an analytical solution of the condensation equation valid for the range of intermediate Knudsen numbers and, by assuming an initial lognormal particle number size distribution, further derived an analytical formula for describing the time evolution of CS. They presented a simple model describing a coupled dynamics between condensing vapors and CS. This model gives reasonable predictions of the CS dynamics during the periods of the aerosol growth by condensation in the atmosphere. Additionally, Mazon et al. (abstract in this collection) started analyzing the effect of forest canopy on the ion sink using vertical ion distribution measurements.

**Planetary boundary layer, vertical and horizontal mixing**

Planetary boundary layer (BL) plays a crucial role in weather, air quality and climate change research. Manninen et al. (manuscript in preparation and abstract in this collection) developed a stand-alone and site-independent classification method for Doppler and wind lidars. The method enables the identification of the main drivers for mixing with the BL with a temporal and spatial resolution of a few minutes and tens of meters, respectively, and it enables classification of BL types. The continuous and long-term observation dataset, created with our method, allows the evaluation of boundary-layer type parameterization schemes in different climate models. Sillanpää et al. (abstract in this collection) investigated the relation between the planetary boundary layer height (PBLH) and different radiation variables based on data obtained from the SMEAR II station in Finland. The aim of this work is to develop a proxy for PBLH using radiation variables and possible other common meteorological variables.

Nikandrova et al. (abstract in this collection) combined aircraft measurements and lidar data to investigate the vertical distribution of aerosol properties between the ground and cloud layers. In most cases, one or two layers with different aerosol and meteorological characteristics above the boundary layer (BL) could be observed. Aerosol number concentrations in all size ranges were usually the highest in the BL. The shape of the size distribution in the upper layer(s) were often similar to those in the BL, but with overall lower concentrations due to dilution of particles into a large volume of air. The interface between the BL and upper layer(s) showed aerosols properties that were often some combination between these layers.
The impacts of air mass history on the particle number concentrations observed at SMEAR I station in Värrö were analyzed by E.-M. Duplissy et al. (abstract in this collection). They showed that the longer air masses spend over the sea ice, the lower aerosol number concentrations are. Additionally, they showed that aerosol concentrations correlate with North Atlantic Oscillation and Arctic Oscillation –indices.

Aerosol-radiation and aerosol-cloud interactions

Severe air pollution episodes have been frequent in China during the recent years, yet the ultimate cause for the most severe episodes has remained unclear. By combining a new theoretical framework with ambient observations and model simulations, we showed that high concentrations of particulate matter enhance the stability of an urban boundary layer, which in turn decreases the boundary layer height and consequently cause further increases in aerosol concentrations (Petäjä et al. 2006). We further showed that this feedback mechanism is most efficient at high ambient black carbon concentrations (Ding et al. 2016). Our analysis explains why air pollution episodes are particularly serious and severe in megacities, and during the days when synoptic weather conditions stay constant.

Khansari et al. (abstract in this collection) studied a feedback mechanism combining both the upper and lower branches of the COBACCI feedback loops (Fig. 1). They investigated the correlation between temperature and the ratio of diffuse and total radiation during clear-sky conditions in Hyytiälä based on in-situ data and further with radiation data derived from satellite retrievals. The results show that the lowest observed diffuse to total radiation ratios increase with temperature, implying that the biogenic SOA formation sets a temperature-dependent minimum level for the radiation ratio.

The study by Tabakova et al. (abstract in this collection) reveals the impacts of CCN concentration and dry air entrainment levels on the cloud droplet radius in warm single-layer non-precipitating clouds at the SMEAR II station. The observations gathered with W-band ARM Cloud Radar and microwave radiometer were applied to quantify the decrease of droplet growth with increasing CCN concentration and increasing dilution.

Liu et al. (2017) investigated aerosol effects on warm cloud properties using multi-sensor satellite observations. They found that with an increasing aerosol load measured by the aerosol optical depth (AOD), the cloud droplet effective radius first decreased and cloud fraction increased, as one would expect based on the first aerosol indirect effect. However, when AOD reached values of about 0.3–0.4, an opposite relation between AOD, cloud droplet size and cloud fraction started to emerge. The influence of aerosols on cloud properties was found to be dependent on ambient relative humidity and thermodynamic and dynamic conditions in the boundary layer.

Integration and large-scale applications

Pan-Eurasian Experiment (PEEX) Program (https://www.atm.helsinki.fi/peex/) is an international, multi-disciplinary, multiscale bottom up initiative established in 2012, the main focus of it is to solve interlinked global environmental challenges influencing societies in the Northern Eurasian region and in China (Lappalainen et al. 2016). During the past year, a number of scientific research papers have been submitted and published in the PEEX Special issue in the Journal of Atmospheric Chemistry and Physics (http://www.atmos-chem-phys-discuss.net/special_issue265.html). The special issue is continuing the Science Plan process and is serving as a primary platform collecting PEEX relevant scientific results for the periodic PEEX science assessment.

The management of the dataflow from the SMEAR stations is being developed by Rusanen et al. (abstract in this collection) in order to match the requirements of more SMEAR or SMEAR-type stations in future. The SMEARCORE data management and analysis system will document the current practices and simplify setting up new stations and campaigns. The SMARTCORE system will include separate
subcomponents for data collection from the measurement computers, for data storage and indexing, and for routine-like data analysis.

Together with our Chinese colleagues, we reviewed the current knowledge about aerosol pollution over China and the effect of control policies (Wang et al. 2017). The aerosol properties covered in that work were the particle mass and number concentration, particle chemical composition, and particle number size distribution.

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ACTRIS - AEROSOLS, CLOUDS AND TRACE GASES RESEARCH INFRASTRUCTURE

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WHY IS ACTRIS BEING IMPLEMENTED

Aerosols and other short-lived atmospheric forcers (SLCF) play an important role in climate change, air quality and health issues all over the world (e.g. IPCC, 2013, Petäjä et al. 2016, Lelieveld et al. 2015). They require careful observations, scientific research and deep understanding in order for humankind to solve the grand challenges we are facing (Kulmala 2015, Lappalainen et al. 2016). The SLCFs remain in the atmosphere only for a short time, which makes their concentrations and properties very variable in both time and space. Therefore, measurements limited to a short time period or to one location do not give a representative picture of them. There are a number of measurement stations in the world with atmospheric aerosol time series extending for more than a decade (e.g. Hari and Kulmala, 2005, Asmi et al. 2013, Nieminen et al. 2014). In some areas, such as Europe, the number and spatial coverage of those stations is enough to create a representative network. The same situation applies to cloud microphysics and reactive trace gases. To make these networks truly functional and to maximize their benefits to science, they need to be well coordinated and to have a stable funding scheme.

International Research Infrastructures are a tool for enabling implementation of scientific instruments that are too big for any single nation to build alone. They also enable a more continuous funding scheme for large-scale international operations. ACTRIS (Aerosols, Clouds and Trace gases Research Infrastructure) is a European research infrastructure for observing the short-lived components of the atmosphere, and for enabling more high-level research in these fields. The general idea in ACTRIS is to pool together the efforts around Europe in order to achieve better results than any nation alone would achieve (Figure 1). It is worth pointing out that the role of ACTRIS is to support science, not to make science. ACTRIS will not do research, but will provide various services that will enable researchers to produce better scientific results.

Figure 1. The general concept of ACTRIS
ACTRIS provides numerous services to the scientific community and to other users:

- The main service of ACTRIS is to provide atmospheric measurement data from the numerous ACTRIS-affiliated measurement stations around Europe and also in other areas. The data will be freely available via ACTRIS Data Centre. The data is inter-comparable due to common measurement and data processing protocols, and quality controlled with regular obligatory calibrations of the instruments.
- Another ACTRIS service is to provide supported access to the most prominent observatory sites and atmospheric simulation chambers. This way the most promising research projects will always have access to the best facilities and expertise available.
- Besides data delivery, the Data Centre provides virtual tools for processing the data online.
- ACTRIS also provides training and education related to instruments and atmospheric data processing.

**HOW IS ACTRIS BEING IMPLEMENTED**

ACTRIS comprises of Central Facilities and National Facilities. The Central Facilities are Head Office, Data Centre and six Topical Centres for calibration of measurement instruments and expertise in different fields of ACTRIS. There will be six of these Topical Centres:

- In situ Aerosol Centre
- Remote sensing Aerosol Centre
- In situ Cloud Centre
- Remote sensing Cloud Centre
- In situ Reactive Trace Gases Centre
- Remote sensing Reactive Trace Gases Centre

The National Facilities are the numerous measuring sites, research chambers and laboratories producing atmospheric data. Most of these facilities exist already, but some upgrading of the sites is expected to be needed in order to reach the data and procedure standards of ACTRIS.

ACTRIS has been adopted on the European roadmap of new research infrastructures in 2016, and is expected to start its operations in 2020 and to be offering its services in full capacity in 2025. ACTRIS has not set an expiry date, but instead plans to develop as the instrumentation develop and the user community needs may change. The schedule of ACTRIS is presented in figure 2.

![Figure 2. The schedule of ACTRIS and EC-projects supporting the implementation](image)

As the expected legal and organisatorial model of ACTRIS is expected to be ERIC (European Research Infrastructure Consortium), the members of ACTRIS will be the countries hosting ACTRIS facilities. Currently there are 21 countries involved in the preparation of ACTRIS. 12 of these have given their political support for the process and become members of Interim ACTRIS Council (IAC), and three more are observers in IAC. The remaining six countries have not given a political statement on ACTRIS, but have institutions participating in the preparation of the infrastructure. The participating countries and their level of commitment are given in Figure 3.
Currently the ACTRIS-activities around Europe are funded by long-term- and project based national funding, and by project-based European Commission (EC) funding. When ACTRIS becomes its own legal entity, this will change. As the members of ACTRIS will be the countries, they will also be the funders of the infrastructure. The states commit themselves to fund their share of the national and international ACTRIS activities for five years at the time, and gain advantage to their scientific community via ACTRIS.

The membership fees for the envisaged ACTRIS ERIC will be used for covering the part of the Central Facility costs, and for supporting access of users to the Topical Centres and to selected National Facilities. This supported access applies to researchers from the member counties, given that the quality of their planned research is rated high enough by a review. Private sector users and researchers from non-membership countries will need to pay a user fee to cover their costs to the infrastructure.

At the moment, the international coordination activities of ACTRIS are funded via three EC-funded projects: ACTRIS-2, EUROCHAMP 2020 and ACTRIS PPP (Figure 2). ACTRIS-2 focuses on scientific integration of the research communities around atmospheric aerosols, clouds and trace gases, and provides funding for trans-national access to 18 research facilities around Europe. EUROCHAMP 2020 does the same for research with atmospheric simulation chambers around Europe. ACTRIS PPP is a project to prepare the governance, legal, financial and operational frameworks needed for the fully fledged research infrastructure organisation.

Finnish partners are involved in all three projects, and in general the Finnish role in ACTRIS is significant. Finnish Meteorological Institute (FMI) and University of Helsinki (UHEL) are leading ACTRIS PPP, and Finland is preparing to host ACTRIS Head Office in Kumpula, Helsinki. FMI also plans to host one part of ACTRIS Data Centre (Cloudnet data) and UHEL is planning to host parts of Reactive Trace Gases Topical Centre (ELVOC) and Aerosol In-situ Center (nanoparticle and cluster
measurements). Besides FMI and UHEL, also University of Eastern Finland (UEF) and Tampere University of Technology (TUT) are contributing to ACTRIS. Together the Finnish institutes expect to include in ACTRIS several measurement sites, one simulation chamber (UEF) and one mobile laboratory (TUT).

EFFECT OF ACTRIS

In the ACTRIS vision the nature of atmospheric research will be different than it is today. The continuous atmospheric measurements will be performed and maintained by scientific engineers focusing on that task, and researchers around the World will use ACTRIS data for their research. This arrangement will free the researchers from operating and seeking funding for the long-term measurements, and grant them more time for utilising the data. Measurement campaigns and novel measurements will still be performed by the research scientists with the help of the station personnel at ACTRIS stations.

The free availability of high quality data with wide coverage, and the access to best facilities and expertise in Europe will give the European atmospheric science a competitive edge over other regions. The availability of the data will also allow new services to be built on the data. Besides publicly funded research, access to ACTRIS facilities will also be available for commercial actors, which will enhance the public-private collaboration and lead to new science-based innovations.

ACKNOWLEDGEMENTS

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For more information about ACTRIS, please visit www.actris.eu.

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RESEARCH ACTIVITIES OF THE ATMOSPHERIC MODELING GROUP AT THE ATMOSPHERIC RESEARCH CENTRE OF EASTERN FINLAND

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Keywords: AEROSOL, CLOUD, MODELING, FORCING, AEROSOL-CLOUD INTERACTIONS

INTRODUCTION

The research focus of the Atmospheric Modelling group at the Atmospheric Research Centre of Eastern Finland is on atmospheric composition, particularly atmospheric aerosol particles, their effects on climate, health, and air quality. The group has been very much model development oriented laying its ground on the aerosol module SALSA which was originally developed to be used in global scale models and has been implemented in the air quality model MATCH (Andersson et al., 2015), and the aerosol-chemistry climate model ECHAM-HAMMOZ (Bergman et al., 2012; Kokkola et al., 2017). More recently, the group has worked on its implementation in a cloud resolving model UCLALES (Stevens et al., 1999; Tonttila et al., 2017) with latest addition being the inclusion of semivolatile compounds. On top of this, the model can be used for box model studies for example simulating chamber experiments.

The role semivolatile compounds such as ammonia, nitrate, and secondary organic aerosol (SOA) have been acknowledged to significantly affect the hygroscopic mass of aerosol. Thus they affect the aerosol size, their radiative properties, and their ability to form cloud and fog droplets. Already 20 years ago, it was hypothesized that in polluted conditions semivolatiles can form droplets that can be considered activated even in subsaturated conditions (Kulmala et al., 1997). However, the ability to properly model such processes in the large scale has been missing and UCLALES-SALSA provides a novel model framework to investigate the aerosol-cloud interactions of semivolatiles for the first time (Kudzotsa et al., 2017, in preparation). We have implemented ammonia and nitric acid condensation and evaporation as well as a semivolatile SOA formation mechanism which separates organic aerosol formed in the gas phase to volatility classes, in other words, uses the volatility basis set approach. Applying the global model, we have studied how the role of biogenic aerosol changes in changing climate (Mielonen et al., 2017, in review).

PROCESS SCALE

Although the focus of the modelling group is in the cloud and the global scale, the group has been involved in chamber studies and doing 0-dimensional model simulations with SALSA. The group has been involved in the CERN CLOUD chamber studies, which investigate different aspects of nucleation and new particle formation in the atmosphere (Gordon et al., 2017). SALSA has
CLOUD SCALE

The gap between process scale and global scale studies is massive since the scales in process scale are in micrometers while global scale models have spatial resolution of the order of 100 km. To fill in this gap, we have started using the abovementioned large eddy simulations model UCLALES, which can be used in simulating processes occurring in the sub-grid scale of a global scale model (Tonttila et al., 2017). The model includes all aerosol microphysical processes together with cloud activation of the aerosol, ice nucleation, melting, and deactivation of cloud droplets. Figure 1 shows the schematic of the model. It is really a state-of-art model, especially in its description of aerosol processes. It is one of the most advanced aerosol schemes in LES models and provides an excellent platform for taking process knowledge from the Center of Excellence to the global scale.

The model has been applied to improving the UK Met Office numerical weather prediction model UKV (Boutle et al., 2017, in review). UCLALES-SALSA model was used to estimate the number of droplets in a long persisting fog. UKV has a prescribed concentration for droplets, which, according to our LES simulations, was found to be too high a number and the fog properties were incorrectly forecast. Correcting the UKV model using the LES simulated droplet concentrations, UKV showed a significant improvement in its capability to forecast long persisting fog episodes.

GLOBAL SCALE

The group has been a major contributor to the development of aerosol-chemistry-climate model ECHAM-HAMMOZ for the past 11 years being in the consortium which jointly develops and distributes the model. Recent developments include new scheme for SOA formation. This scheme has been coupled to the chemistry model MOZ, which provides the gas phase and heterogeneous chemistry for the gas phase oxidation of biogenic volatile organic compounds.

With this model framework, we have studied the possibilities and drawbacks of artificially affecting climate change by stratospheric sulfur injection in order to produce long persisting stratospheric...
aerosol which would cool the climate (Laakso et al., 2016). In addition, the plausibility of optimizing the injection strategy was investigated (Laakso et al., 2017).

Our group has also combined global modelling with remote sensing observations in a study where we investigated if biogenic organic carbon emissions which increase with temperature can have a significant effect on aerosol direct radiative forcing in a warming climate. In order to do this, we developed a method, which can extract information of biogenic aerosol from satellite data by filtering anthropogenic contribution to aerosol optical depth using tropospheric NO₂ concentrations. This was achieved using data from the remote sensing instrument OMI. To complement satellite observations, we implemented a volatility basis set based biogenic secondary organic aerosol formation scheme in ECHAM-HAMMZ. These methods combined showed that biogenic organic aerosol can significantly affect aerosol direct effect when the climate warms (Mielonen et al. 2017, in review).

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THE JOINT INTERNATIONAL RESEARCH LABORATORY OF ATMOSPHERIC AND EARTH SYSTEM SCIENCES BY NANJING UNIVERSITY AND THE UNIVERSITY OF HELSINKI

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Keywords: JirLATEST, SORPES, Global SMEAR, Nanjing, China

INTRODUCTION

The Joint International Research Laboratory of Atmospheric and Earth System Sciences (JirLATEST) is a joint research infrastructure by Nanjing University and the University of Helsinki. JirLATEST is based on the Station for Measuring Ecosystem-Atmosphere Relations (SMEAR) station concept and part of the Global SMEAR network. JirLATEST focus on the atmospheric and earth sciences, to advance science frontiers and to meet China’s national development needs.

AIMS

The JirLATEST aims at key scientific issues in the field of atmospheric and earth system science. Collaboration will jointly develop earth system observation platforms in China, based on scientific knowledge obtained from the Station for observing Regional Processes of the Earth System (SORPES) that is the first SMEAR concept station in China. Long-term concurrent observation, synthesis data analysis and modeling development are the base for scientific outcomes. The JirLATEST will focus on improving the current understanding to land-atmosphere interactions under different environment, and will also reveal the interactions and influence mechanisms of human activities on the physical, chemical, and biological processes in the earth system. Based on these efforts, the JirLATEST could substantially support the needs for tackling climate change, air pollution and other disasters, and meanwhile train next-generation cross-disciplinary talents.

JirLATEST has four main focus areas:

a) Land-Atmosphere Interactions: Processes and mechanisms. With a focus on energy balance, cycles of water and chemical compounds and on land ecosystem and atmospheric boundary layer.

b) Anthropogenic impacts on land-atmosphere interactions. With a focus on the control processes and their interactions of atmospheric aerosols and land use/land cover change, including urbanization, influenced by human activities.

c) Improvement of parameterization schemes of Earth System Models. With a focus on improving parameterization schemes of key physical and chemical processes in the Earth System Models, including air quality models, based on new findings from field measurement.

d) Forecast, assessment, and policy making for air quality, weather/climate. With a focus on air quality and weather/climate forecast, impacts assessment and making policy based on improved models.

FUTURE PROSPECTS

The collaborations between two sides have been centered in observations in SORPES. Since 2009, SORPES has developed into an integrated, comprehensive observation station for studying land surface processes, air pollution-
climate interactions, ecosystem-atmosphere interactions and hydrological processes and water cycle. With the support of SMEAR, observations in SOPRES have focused on the measurement of physical, chemistry and optical properties of aerosol and aerosol precursors, and high-quality continuous observational data has been accumulated since 2009. This has led to more than twenty important publications through the collaboration between scientists from both sides and to education activities such as first Autumn School between the Nanjing University and the University of Helsinki held on October 2017.

To fulfil urgent requirement of Chinese Government for solutions to face Grand Challenges, the JirLATEST will focus on the following four challenges:

1) Land-surface processes
2) Atmospheric chemistry-climate interaction
3) Land ecosystem-atmosphere interaction
4) Hydrology and water cycle

JirLATEST will be used to improve current understanding of these processes and their interactions, and of knowledge on energy, material and water cycles in the Earth System through an integrated analysis based on these observations.

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HAZE BEIJING BY BEIJING UNIVERSITY OF CHEMICAL TECHNOLOGY AND THE UNIVERSITY OF HELSINKI

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Keywords: HAZE Beijing, Global SMEAR, Beijing, Peking, China

INTRODUCTION

The rapid, large-scale urbanization and industrialization of China are unique in history. Consequently, China’s air pollution situation has worsened dramatically during the last 2–3 decades as emissions from industry, energy production and traffic have increased. Highly non-linear processes, such as atmospheric chemistry and aerosol dynamics, can transform the urban pollution cocktail, Chemical Cocktail (Kulmala 2015), and generate secondary pollution, such as ultrafine particles and ozone. The fact that new particle formation can occur in polluted Chinese megacities like Beijing, suggests that there are several major physical and chemical mechanisms in a heavily-polluted atmosphere that have not been recognized before.

To understand the processes behind the haze phenomenon in mega-city like Beijing, it is crucial to make long-term, continuous and comprehensive observations on aerosol particles, trace gases and atmospheric oxidants (Kulmala et al., 2015). Recent advancements in theoretical understanding has made it possible to explain how enhanced pollution decreases atmospheric turbulence and mixing, reducing the boundary layer height and causing further enhancement of pollution levels (Petäjä et al., 2016). These recent advancements, together with local government support, provide platform to clarify the Chemical Cocktail of Beijing.

AIMS

By quantifying the processes, interactions and feedbacks within different air pollutants and ambient conditions, HAZE Beijing project can determine the most efficient steps towards reducing secondary air pollution, and thus clean the Beijing city air. The main focus will be on secondary pollution like new particle formation (NPF) and gas-to-particle conversion, since NPF can produces more than 60% of aerosol number load in very polluted megacities (see Kulmala et al., 2016b).

Main scientific question to answer is:

• What are the key processes related to gas-to-particle conversion and atmospheric boundary layer (BL) dynamics in heavily-polluted environments?

Answers will provide crucial knowledge to:

a) why atmospheric new particle formation (NPF) occur in heavily-polluted conditions where the ratio between the condensation sink and particle growth rate is approximately 10 times too high in order to be explained with present knowledge.

b) how are Boundary Layer (BL) dynamics and formation of the chemical cocktail in the BL interacting with each other?

c) are there new and effective oxidation pathways?
d) what are the relative role of different compounds, such as inorganics, organosulphates, organonitrates and other organic compounds, in participating atmospheric gas-to-particle conversion (GTP) and NPF?
e) how is black carbon and other particulate matter affecting the stability of BL?

FUTURE PROSPECTS

HAZE Beijing will rely on continuous, comprehensive observations of atmospheric composition and fluxes combined with detailed description of meteorology. This research ideology has been proven in SMEAR II (Station for Measuring Earth system–Atmosphere Relations, Hyytiäälä, Finland). The SMEAR network was extended to the city of Helsinki, Finland, in 2005, when SMEAR III (Järvi et al. 2009) was established to examine the urban environment. Knowledge from both SMEAR II and III are the backbone in HAZE Beijing.

The measurements in Beijing and in Finland provide a unique basis to diversify the existing aerosol, trace-gas and GHG measurements into different environments which, besides enhancing our scientific understanding, will provide crucial information for regional air quality models, basis for education activities and decision making process in national and local levels. HAZE Beijing can also find out long-term changes and trends in China. With combined efforts, HAZE Beijing is able to connect atmospheric data with surface data and to find out combinations and trends that have not been discovered during earlier research campaigns in Beijing.

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PAN-EURASIAN EXPERIMENT (PEEX) PROGRAM - OVERVIEW AND FUTURE PROSPECTS

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Keywords multidisciplinary approach, multiscale research, global grand challenges, arctic-boreal environment, observation networks, modelling platform, land-atmosphere interactions, the Arctic Ocean

BACKGROUND

Pan-Eurasian Experiment (PEEX) Program (www.atm.helsinki.fi/peex/) is an international, multidisciplinary, multiscale bottom-up initiative. The precursor idea of the Eurasian Pan-Eurasian Experiment (PEEX) was introduced by Kulmala et al. (2011) addressing the importance of land-atmosphere dynamics of Siberian boreal forests for the climate system. The first idea was to organize so called Pan-Siberian experiment, a measurement program for aerosols, Greenhouse gases (GHG) and biogenic volatile organic compounds (BVOCs). Within this activity, an establishment of a coherent, coordinated observation network from Scandinavia to China, together with a science program focused on understanding processes in the land-atmosphere interface was preliminary discussed. In 2012, this idea expanded to cover the whole Northern Eurasian geographical domain and China, and evolved into the Pan-Eurasian Experiment (PEEX) (Kulmala et al. 2011, Lappalainen et al. 2014, 2015).

STATE-OF-THE-ART AND FUTURE CHALLENGES

The promoter institutes of PEEX are: University of Helsinki and Finnish Meteorological Institute in Finland, Institute of Geography of Moscow State University, AEROCOSMOS, and Institute of Atmospheric Optics (Siberian branch) of the Russian Academy of Sciences (RAS) in Russia, Institute of Remote Sensing and Digital Earth (RADI) of the Chinese Academy of Sciences (CAS) and Institute for climate and global change research of Nanjing University in China. The program governance and the communications is coordinated by the PEEX Offices in Helsinki (PEEX Headquarters, PEEX-HQ), Moscow, Nanjing and Beijing under the guidance of the Program Steering Committee. In 2018, the office network is expected to expand and new offices and/or local contact points will be established in Vladivostok and in Tyumen. The upcoming challenge will be education of the new PEEX science officers working as the local contact points and establish fluent information flows within the network.

At an institutional level, the collaboration within PEEX is typically initiated via signing a Memorandum of Understanding (MoU) with the PEEX program. At the moment we have signed PEEX oriented MoUs with 30 universities and research institutes in Russia and 5 in China. As a whole the PEEX researchers’ network includes approximately 4000 researchers from 20 countries from Europe, Russia and China. The PEEX science conferences are the main forum for research community to share their scientific outcomes. In addition to organization of the conferences, the active work of the PEEX working groups (WG) is facilitated. So far, the Modelling-Platform WG and the Infrastructure WG have been the most active and their work has been mainly focusing on the concept design of the modelling platform and on establishing the PEEX in-situ observation network in Russia. New working groups and community based activity as bottom-up activities are foreseen on topics like “environmental change and epidemics” and “connecting social parameters to atmospheric emissions”.

PEEX-HQ is coordinating the PEEX network at different levels (researchers, institutes and organizations) and the governance activities together with other offices in Russia and in China. This work is facilitated by different tools such as a website (www.atm.helsinki.fi/peex/), e-news, e-mailing lists, organization of conferences, conference sessions, meetings and forums (e.g. 1st Sofia Earth Forum in Helsinki 2016). In 2012-2017, we have organized altogether 7 meetings and 3 science conferences (Helsinki 2015, Beijing 2016, Moscow 2017). Starting from January 2017, PEEX has joint the U-Arctic community of 170 Arctic universities and PEEX acts as a “Arctic-Boreal Hub”, which is one of the U-Arctic Thematic networks (www.uarctic.org/organization/thematic-networks/arctic-boreal-hub/). The Arctic-Boreal Hub – network expands the PEEX approach into a circumpolar context and opens up connection points with the US and Canadian research communities. One practical example of this activity was the ARCTIC Fluxes – CRAICC/Crucial (Critical steps in understanding land surface – atmosphere interactions: from improved knowledge to socioeconomic solutions) workshop with 71 participants from Canada, USA, Europe and Russia, organized in February 2017 in Hyytiälä, Finland. As a whole, the PEEX network is open for new researchers and organizations representing different scientific disciplines to join in and is especially interested in strengthening the role of social and socio-economic sciences within this community.
The main scientific mission of PEEX program is to understand large-scale feedbacks and interactions between the land-atmosphere-ocean continuum in the changing climate of the Northern high latitude and in China (Kulmala et al. 2016, Lappalainen et al. 2016). The PEEX Science Plan (Lappalainen et al. 2015) addresses the scientific aims and large-scale research questions of the program. The focal points in the PEEX research are e.g. on the net effects of various feedback mechanisms connecting the biosphere, atmosphere and human activities. Such feedbacks stem from higher temperature and increased concentration of greenhouse gases (GHG) in the future. The climate change and associated feedbacks lead to further consequences, such as permafrost thawing, land cover changes, increased dissolved organic carbon content in freshwaters, acidification of the Arctic Ocean, increased photosynthetic activity, elevated GHG uptake by terrestrial ecosystems, increased Biogenic Volatile Organic Compound (BVOC) emissions, secondary aerosol, changes in cloud processes and alterations in the radiation budget. These feedbacks can either hinder or speed up the climate change.

The backbone of the research approach has been the scientific contribution of the Finnish Center of Excellence in Atmospheric Science - From Molecular and Biological processes to The Global Climate (FCoE-ATM), which delivers ca 150-200 peer reviewed papers annually. In addition to FCoE –ATM, a new 5 year European Research Council’s Advanced Grant project on “Atmospheric Gas-to-Particle Conversion” and the Academy professorship “Air quality - climate interactions and feedbacks” lead by Academician M. Kulmala will continue the scientific work relevant to the PEEX research agenda. Starting from 2015 PEEX is also gathering research results on the Arctic-boreal environments via the PEEX Special Issue in Atmospheric Chemistry and Physics (ACP) scientific journal (www.atmos-chem-phys.net/special_issue395.html). Altogether 28 papers in a final form and 10 papers under revision have been published by August 2018. Based on the keywords listed in the papers, the foci of the results has been on the role of boreal forest and their BVOC emissions and subsequent aerosol formation processes (Fig.1). The future challenge is to expand the scientific coverage of the published results relevant to PEEX research agenda and, in practice, initiate the research collaboration with socio-economic research communities.

Figure 1. The coverage of the PEEX research fields is based in the articles in the PEEX special issue in ACP that are already published by August 2018. There are 28 published. The 10 papers under revision are not included here. In the following networks, the size of the circle refers to the amount of papers, the position of the circles indicates the degree of relation while the colors indicate clusters of more related circles. (Analysis and visualization by Nuria Altimir, University of Helsinki).
The main strategic challenge of the program is to initiate a comprehensive and coordinated research infrastructure in collaboration with the main partners in Russia and in China. There is an urgent need for comprehensive, coordinated in-situ observations over the Arctic and Northern Eurasian region detecting different processes, energy flows, emissions and concentrations between different Earth surfaces (forest, peatlands, lakes, urban) and atmosphere. One of the most important relevant PEEX activity is just started within ERAPLANET (The European network for observing our changing planet) project (the strand-4) called “Integrative and Comprehensive Understanding on Polar Environments (iCUPE) lead by University of Helsinki. The core idea of iCUPE is the development of novel, integrated, quality-controlled and harmonized in-situ observations and satellite data in the polar areas, including also data products to the end users.

The PEEX land-ecosystem in-situ network will be built upon complementary approaches. The coordination and upgrading of the existing station activities and establishing new SMEAR (Stations for Measuring Earth surface - Atmosphere Relations) -typed stations will be based a SMEAR concept (Hari et al. 2016). The principles of the PEEX in-situ observation network, also as a part of the global observatory, are being introduced in Hari et al., 2005, 2009, 2016 and Kulmala et al. 2016., Kulmala et al 2016 (manuscript in preparation). In reference to the “coordination and upgrading of the existing stations” in Russia, the collection of the preliminary information of the existing station activities started in 2012. The first inventory on over 200 in-situ stations operating in the Arctic and Subarctic Eurasian regions was conducted by the Russian Academy of Sciences (RAS) and Moscow State University together with the University of Helsinki (Alekseychik et al. 2016). Based on the first inventory we currently collect more detailed information, here termed as “station metadata”. The station metadata, the detailed descriptions of measured variables and the observation site, enables categorize the stations in a systematic manner and will provide tools to connect them to international observation networks, such as WMO-Global Atmospheric Watch Program, China Ecosystem Network (CERN) and global SMEAR network, and to carry out standardization work towards common data formats. Based on this work, PEEX will also publish a station e-catalog, which will give information on the on-going measurements and contact points and initiates research collaboration between the research groups.

The marine observations from the Arctic Ocean, sea ice and atmosphere, are needed to obtain a better understanding on the state and change of the marine Arctic climate system. The PEEX marine infrastructure activity addresses the Arctic Ocean and adjacent seas. Similarly to PEEX/SMEAR, the PEEX marine component will be based on a hierarchical concept of station network, but affected by the practical challenges in making long-term observations in and over the sea. The processes to be studied include the sea ice thermodynamics and dynamics, ocean heat and freshwater budgets, ocean circulation, waves and tides, ocean chemistry and ecosystems, atmospheric heat and moisture budgets, synoptic-scale cyclones and Polar lows, troposphere-stratosphere coupling, atmospheric boundary-layer processes, as well as aerosols and clouds (Vihma et al., 2014; Vihma et al. manuscript in preparation).

The concept design of the PEEX modelling platform (MP) is also in process and is planned to be published in 2018 (Baklanov et al. manuscript under preparation). The MP will be based a seamless modelling framework from nano-scale modelling to Earth system models. It will also introduce community-based services for data mining and for demonstrating air pollution events at regional scales The large-scale component of PEEX-MP will be consist of ESM EC-Earth (portal.enes.org/models/earthsystem-models/ec-earth-1/ec-earth), which combines all relevant elements of the PEEX domain in a global scale.

As a whole PEEX is an active contributor and a collaborator in the international research and research infrastructure landscape. The main international partners and collaborators as Future Earth (PEEX - FE Partnering Program), Arctic Council (contributing the AMAP and SAON WGs), GEO – GE OSS Cold regions (PEEX - the in situ observations activity), IIASA (Arctic Initiative), iLEAPS and WMO GAW program. PEEX is also closely connected to International Eurasian Academy – European Center and the
DBAR (Digital Belt and Road) Initiative, which are interested in to provide a big data platform on earth observation from China and countries along the new Silk Road - Belt and Road area.

CONCLUSIONS

The PEEX has released the program agenda and is currently finalizing the conceptual design of the PEEX relevant research infrastructures. The program is currently calling for financial support from European Union, Russian and Chinese basic funding organizations to implement the program at the large scale. The implementation of the PEEX program would make significant impact on the sustainable development of the Northern societies and China.

ACKNOWLEDGEMENTS

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OVERVIEW OF THE EARTH SYSTEM MODELING GROUP ACTIVITIES

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Keywords: EARTH SYSTEM MODEL, CLIMATE, GLOBAL MODELS.

The ESM group has a strong background in model development. The development of Earth System Models in recent years has involved new modules of anthropogenic and natural emissions, updating atmospheric chemistry schemes, new modules for aerosol dynamics and aerosol formation, and several other Earth System Components. Furthermore, the ESM group applies models to assess global effects of ATM FCoE processes and interactions, future climate change and anthropogenic impacts.

The main tools of ESM group are three models (Table 1), Max-Planck Institute Earth System Model (MPI-ESM), Norwegian Earth System Model (NorESM) and European Earth System Model (EC-Earth). Furthermore, the group is involved in integrated aerosol-chemistry-weather modeling (Mahura et al., 2017).

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Land-vegetation</th>
<th>Ocean</th>
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<tbody>
<tr>
<td>EC-Earth</td>
<td>IFS</td>
<td>LPJ-GUESS</td>
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<tr>
<td>NorESM</td>
<td>CAM</td>
<td>CLM</td>
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<td>MPI-ESM</td>
<td>ECHAM</td>
<td>JSBACH</td>
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Table 1: Earth System Models used in the group.

Development of Earth System Models

While anthropogenic aerosols have an overall cooling effect on climate, the quantification of the aerosol forcing requires a sufficient knowledge on how to describe human activities and their effect on atmospheric composition. Over the last decades, anthropogenic emissions of aerosols have been described simply as mass flux of selected compounds, e.g. sulfate, black carbon and organic carbon. Recently, with the development of detailed aerosol microphysical modules in climate and air quality models, the mass emissions have been assigned a certain aerosol size distribution. The assumptions on the emission size distribution are usually simplified (e.g. single log-normal mode) and not up-to-date with emerging emission data. The ESM group has implemented a novel size-segregated primary aerosol emission module into ECHAM-HAM model. The results from an initial study with log-normal aerosol microphysics indicate that the detailed size-segregated emissions could lead to improved model bias in terms of accumulation mode particles, which would be significant for anthropogenic indirect effects (Xausa et al., 2017). Further studies with sectional model ECHAM-SALSA will be performed to analyze climate effects in more detail.

The ESM group has developed the nucleation and secondary organic aerosol modules in EC-Earth, NorESM and MPI-ESM. The respective modules in EC-Earth and NorESM will be used in the
Coupled Model Intercomparison Project Phase 6 (CMIP6), working towards that the nucleation and organic aerosol research at FCoE ATM will be included in IPCC AR6 radiative forcing estimates (Makkonen et al., 2017).

Model evaluation

In principle, a global aerosol-chemistry model is a series of hundreds of thousands of box models for atmospheric composition. This poses a challenge in terms of validation, since only a small fraction of individual of the model cells can be directly evaluated against in-situ observations. The ESM group is working towards comprehensive approaches to constraining and evaluating models using multiscale observations from various sources, including in-situ station and aircraft data, satellite and other remote sensing data, as well as suitable proxy data (e.g. deposition profiles).

Terrestrial and marine organic aerosol

Evaluation of global aerosol fields requires not only correlating observed and simulated quantities (e.g. masses, number concentrations), but a holistic understanding of model performance regarding underlying processes. As an example, we have analyzed the performance of ECHAM-HAM in terms of aerosol formation and growth due to biogenic emissions in boreal forest (Rose et al., 2017). The analysis is based on Hyytiälä. We show that ECHAM-HAM is able to fairly reproduce monoterpene concentrations measured in Hyytiälä between 2010 and 2013, as well as the implication of their oxidation products in both early cluster and particle growth towards CCN sizes. Largest discrepancies between measured and simulated variables are observed during the coldest months, and most likely arise from missing monoterpenes sources in the model. Our results are promising since the role of monoterpenes in new particle formation and growth might intensify in the future in boreal forest-like environments, where their sources are expected to increase.

Although the terrestrial sources of organic aerosol have been the key focus of our research for several years, the holistic understanding of global organic aerosol a better understanding of marine sources. The marine system is a source of primary organic aerosols (mPOA) as well as secondary organic aerosol precursors. While marine BVOCs could be of minor importance in terms of global aerosol budget, the mPOA is gaining increasing interest in the climate community. The motivation for better constraints on natural marine aerosol background is clear: the ocean regions are susceptible for changes in aerosol concentrations, and a large natural background aerosol population could limit the effect of anthropogenic perturbations and forcing. We have implemented several novel parameterizations of mPOA into EC-Earth, considering a multitude of oceanic proxies. Keskinen (2017) describes the implementation and results in detail.

Coupled Model Intercomparison Project

Finnish research teams are participating in CMIP simulations for the first time, and ESM group is performing simulations for the AerChemMIP experiments together with FMI and KNMI. This requires centennial scale climate simulations with EC-Earth, including atmosphere, ocean and aerosol-chemistry models. The simulations include piControl, which is an pre-industrial equilibrium state simulation providing reference levels for e.g. anthropogenic perturbations. After reaching a required level of stabilization in piControl, a historical (1850–2014) simulation is branched off of piControl. In addition, UHEL contributes to CMIP6 with several future (−2050) scenario simulations.
National and international collaboration and links to research infrastructures

The ESM group applies and develops three different Earth System Models, which all require strong national and international collaboration. In Finland, the climate modeling activities are done in close collaboration between University of Helsinki, Finnish Meteorological Institute and University of Eastern Finland. Joint publications and projects on climate modeling indicate the clear synergy benefits of combining the national efforts in model development and application.

The group maintains close collaboration with Norwegian groups regarding the development and application of NorESM, participating also in a journal paper towards description of new developments for CMIP6. The collaboration with NorESM partners (University of Oslo, Norwegian Meteorological Institute considers mostly the development of the aerosol and chemistry module, but also other Earth System components (e.g. Raisanen et al., 2017). The EC-Earth collaboration spans a wider range of European partners, since the EC-Earth consortium consists of over 30 partners from more than 10 countries. Regarding EC-Earth development, the main international collaborators are KNMI and University of Lund. The CMIP6 simulations within EC-Earth are performed as a consortium effort, integrating UHEL climate modeling activities closely to several EC-Earth partners. The ESM group is participating the Atmospheric Composition working group of EC-Earth.

The ESM group participates in planning and implementation of the PEEX Modeling Platform, which is an international multiscale and multimodel approach to scientific and societal challenges in the Pan-Eurasian domain. Our group is developing the PEEXView platform, which combines (global) simulated data to PEEX observational infrastructure, and allows visualization and co-analysis of several datasets.

Earth System Models are demanding for computational and data infrastructures. In ESM group, all simulations are performed on CSC supercomputing platforms. The operational computational quota of climate modeling is some million CPU-hours per year, which is accommodated by CSC Grand Challenge projects and normal CSC projects. The models in ESM group generate up to several terabytes of output during one simulation year, hence the postprocessing and analysis workflow is streamlined on CSC data infrastructure, including IDA research data storage infrastructure. At the moment, the ESM group is pursuing a national Earth System Federation Grid (ESGF) node to CSC Pouta virtual machine environment. The ESGF node infrastructure provides an open-access platform to store and distribute climate modeling data, and will be primarily used for CMIP6 datasets.

The ESM group is active in several Nordic platforms. Earth System model co-development and co-application in the Nordic perspective is NordicESM network and Nordic Center of Excellence eSTICCC. During 2016–2017, our group participated in initiating a new Nordic collaboration project NICEST (Nordic Infrastructure Collaboration on Earth System Tools), which is working under the NeIC program. Whereas NordicESM network is designed more towards education and research aspects, the new NICEST project serves as a Nordic platform for e-Infrastructure (ESGF) and ESM competence.

Website of the Earth System Modeling group: http://blogs.helsinki.fi/esm-group

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RESEARCH RESULTS OF THE RADAR METEOROLGY GROUP

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Keywords: mixed-phase clouds, snowfall, cloud radar

CURRENT INFRASTRUCTURE STATUS

The radar meteorology group is utilizing state-of-the-art remote sensing and ground-based instruments to study cloud and precipitation processes. The group operates a dual-polarization C-band weather radar in Helsinki, which is used to study impact of high-impact weather on Helsinki metropolitan area, and the cloud and precipitation measurement site in Hyytiälä. The Hyytiälä site is a part of SMEAR and ACTRIS infrastructures (Petäjä et al., 2016). The main research questions that are addressed using Hyytiälä measurements are: cloud and precipitation formation and lifecycle with the emphasis on ice and mixed-phase cloud microphysics.

The cloud and precipitation radar measurements at the Hyytiälä site have started in 2014 during BAECC (Petäjä et al., 2016). Since the campaign the extensive surface based precipitation were running continuously and the radar cloud profiling has resumed in 2016. In August 2016, the University of Helsinki C-band transportable radar and FMI Ka-band cloud radar were moved to Hyytiälä. In September 2017 and March 2018 this setup will be expanded by a W-band cloud radar and microwave humidity and temperature profiler.

NEW RESULTS

During 2016-2017 the group research focused on secondary ice production (Sinclair et al. 2016; Field et al. 2017), riming (Moisseev et al., 2017; Li et al., 2017), retrievals of snow microphysical properties (von Lerber et al. 2017a; Tiira et al 2016), validation of NASA Global Precipitation Mission snowfall rate estimate (von Lerber et al. 2017b), hydrological applications (Niemi et al. 2017) and detection of severe weather by weather radars (Voormansik et al. 2017). Here a short summary of our findings in quantifying riming effect on precipitation is given.

In mid- to high- latitudes majority of precipitation originates from snow (Field et al. 2015). Ice particles grow by vapor deposition, aggregation and riming. Riming is an important precipitation process, given that a large percentage of cloud systems contain supercooled liquid water. Borys et al. (2003) have shown that in mid-latitude orographic clouds both riming and snowfall rates are affected by anthropogenic aerosol pollution. Saleeby et al. (2013) have further investigated this phenomenon and found that the local aerosol effect on snowfall can be significant, though synoptic conditions may have larger influence. Lohman et al. (2004) shown that the aerosol impact on riming could have climatic implications. Given this potential sensitivity of precipitation and climate, there is a need to quantify how important riming is for surface...
Mitchell (1990) and Harimaya and Sato (1989) have shown that riming could explain 30% to 100% of surface snowfall mass. To quantify the impact of riming on precipitation in Finland, 22 snowstorms that took place in 2014-2015 were studied. It was found that riming is responsible for 5 to 40% of snowfall mass.

The proposed analysis also allows to study how cloud precipitation processes as documented by cloud radars, lidars and microwave radiometers affect rime mass fractions of ice particles.

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AN INTRODUCTION TO
INTEGRATIVE AND COMPREHENSIVE UNDERSTANDING ON POLAR ENVIRONMENTS
(ICIPE)


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KEYWORDS:

INTRODUCTION

The polar areas are facing rapid changes in the coming decades (Overland et al., 2013; Ford et al., 2015). Driven by demographic development and globalization, particularly the Arctic societies are facing several grand challenges, such as air, soil and water pollution, climate change, higher demand for resource extraction in these regions, increased anthropogenic emissions due to year-round shipping in the seas of the Arctic Ocean, and other local sources, and long-range transported pollution from Europe, Asia (Russia, China, India), and North America (e.g. Buixade Farré et al. 2014) These activities will put the fragile Arctic environment and the population living in this area in a vulnerable position. The changes will pose unpredictable consequences on food chains, biodiversity and the primary production of different plant
ecosystems and ecosystem capacity to recover from the pollution exposure and environmental changes (e.g. Arnold et al. 2016).

The future warming of the Arctic will affect demographic trends by increasing urbanization and migration to northern regions, and by accelerating changes in societal issues and air quality. One major consequence of warming in the northern latitudes is related to changes in the cryosphere, including the thawing of permafrost and the Arctic Ocean becoming sea ice free part of the year (Kokeli et al., 2017; Meier et al., 2014). This will accelerate global trade activities in the Arctic region if the northern sea route is opened for shipping between the Atlantic and Asia’s Far East. Northern ecosystems and Arctic regions are a source of major natural resources such as oil, natural gas and minerals. The availability and exploitation of natural resources depends also on how significantly the permafrost thaw will damage existing infrastructure.

Human activities have had a profound impact on the composition of the atmosphere and the pollution in the environment through the introduction of ever increasing quantities of heavy metals and other trace elements (Barbante et al. 2001), radioactive nuclides (Ezerinkis et al. 2014), synthesized organic compounds (Hermanson et al. 2010), aerosols such as black carbon (McConnell and Edwards, 2008), trace gases and greenhouse gases. Anthropogenic contaminants can be transported over long distances and accumulate into polar areas. Persistent Organic Pollutants (POPs, such as Polybrominated Diphenyl Ethers, PBDE, Polycyclic Aromatic Hydrocarbons, PAH, Polychlorinated Biphenyl, PCB and persistent Contaminants of Emerging Concern, CEC, Sauve and Desrosiers. 2014) are rarely produced in the Arctic, but have been found in Arctic wildlife, lake sediments as well as annual snow and ice (Herbert et al. 2005, Ma et al., 2011, Seki et al. 2015). Mercury and other heavy metals, such as As, Cd, and Pb, are considered toxic at any level. Their presence is generally determined by local geochemistry, but they can be emitted by human activities resulting in their increased abundance in the polar areas (Barbante et al. 2001, Zheng et al. 2015, Angot et al. 2016). Black carbon (BC), a fine component of almost pure carbon from incomplete combustion, is able to modify the snow albedo by absorbing incoming solar radiation (Jiao et al., 2014). Human activities are impacting the net abundance of these pollutants in the atmosphere, but there is a lack of data exploring the deposition patterns and the abundance of anthropogenic contaminants in polar areas. We also need an improved understanding about their redistribution into different environmental spheres including the biota of the Arctic and Antarctic and the full life cycle of these pollutants (Wöhrnschmimmer et al. 2013).

Local emissions make currently only a small contribution to atmospheric loadings of various pollutants in polar areas, but this might change in the near future as Arctic ice-free areas will extend and more extensive Arctic shipping will become possible (Corbett et al., 2010). Nevertheless, air pollutants from other areas in the world do reach high Arctic regions and have been estimated to have significant impacts on the regional ecosystem and climate (Di Pierro et al., 2011; Breider et al., 2014). Knowledge about source contribution of atmospheric pollution is very limited and further efforts in terms of detailed source identification are urgently needed to formulate and settle mitigation strategies (e.g. Law et al. 2014). The measurements of short-lived climate pollutants, and their precursors, are necessary for evaluating the impacts of increased regional and international activities, e.g. in relation to natural resource extraction, especially in fragile Arctic environments. Correspondingly, similar activities need to be carried out in Antarctica which has a minimal amount of anthropogenic influences and can provide clean reference observations.

In relation to comprehensive in-situ observational capacity, the existing observational networks for the measurements of atmospheric concentrations of air pollutants extend to Arctic and Antarctic environments (e.g. Uttal et al. 2016). However, there are still large gaps in the current measurement networks (Lappalainen et al. 2016), and the interaction between the networks, made up of different national activities, needs to be improved. In summary, the methodology of data acquisition, data quality control and future strategies on data flows and data streams are not harmonized on either the European or global scale. Furthermore, particularly in the polar areas, measurements are not always continuous but often carried out campaign-wise due to economic, environmental or logistical challenges. Polar activities are
often based on national activities and missing synergistic benefits of co-operation in the challenging environments.

Monitoring the surface variations in the Arctic region is a powerful tool to assess the impacts of changes induced into this vulnerable environment. The distribution of different type of land cover (snow, ice, vegetation, soil) can be efficiently analysed using optical data obtained from the new satellite missions merged with data collected during field campaigns and data acquired from cooperative observer networks. In particular, different patterns of snow cover (as well as soil and vegetation cover) exercise considerable influence on the surface energy balance, since variations in land cover change the surface albedo. While there are established methods for retrieving basic variables, changing snow and ice surfaces and ice-free areas are still challenging and the large variability of system itself is limiting the accuracy of such retrievals (Bokhorst et al. 2016). New Sentinel series of Copernicus sensors in the orbit make it possible to retrieve improved land surface variables due to increased capacities in terms of spatial, temporal and angular observations. As a consequence, new Earth Observation (EO) technics will lead to multi-mission time series needed for data assimilation into models of the Earth system compartments in the Arctic.

In summary, in order to address the current state of the environment in the polar areas and to provide fact-based decision-making tools for the society in the future, comprehensive high quality observations of atmospheric concentrations of aerosols, trace gases and related physical variables (atmosphere, ecosystem) from in-situ observations are required in concert with EO from space (Petäjä et al. 2014, Hari et al. 2016). The EO data can be used to study the interactions between different type of surface and the atmosphere. The results obtained allow us to evaluate the impact of pollutants on the equilibrium of the Arctic system and provide an important input for the evolutionary scenarios of Arctic environment. The picture needs to be harmonized and supported with complementary multi-scale modelling (e.g. Kulmala et al. 2011). The vision driving iCUPE activities is that we need to establish and maintain long-term, coherent and coordinated observations and research activities on environmental quality and natural resources in polar areas. The core idea of iCUPE is the development of novel, integrated, quality-controlled and harmonized in-situ observations and satellite data in the polar areas, as well as data products to the end users.

OBJECTIVES AND EXPECTED OUTCOMES

The iCUPE project answers to "The European network for observing our changing planet" (ERAPLANET) thematic strand 4 (Polar areas and natural resources). By combining integrated in-situ and satellite EO with a modelling platform, iCUPE will 1) synthesize data from comprehensive long-term measurements, intensive campaigns and satellites, collected during the project or provided by on-going international initiatives 2) relate the observed parameters to impacts, and 3) deliver novel data products, metrics and indicators to the stakeholders concerning the environmental status, availability and extraction of natural resources in the polar areas. These data, metrics and indicators will be targeted to identified stakeholders. They will be useful for policy development and for improving and clearly communicating our multidisciplinary understanding of the status of the polar environment and pollution dynamics in the future. The knowledge generated is relevant to the general population, policy makers and scientists.

The work in iCUPE will integrate the ground-based and remote sensing observations in a coherent manner, improve accuracy and temporal and spatial resolution of the data and generate novel data products suitable for decision-making and monitoring of the environmental conditions in polar regions.

The existing data and data products, as well as the data and products acquired in the future, will be curated into long-term well-documented databases and made available and ready-to-use for scientists, policy-makers and general public. With an integrated approach, the project will improve our understanding about the pollution sources and sinks, environmental and anthropogenic changes and elements of the cryosphere in polar areas by conducting high-level and high impact research by analysing these integrated data together with the modelling frameworks.
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E-INFRASTRUCTURE FOR ATMOSPHERIC SCIENCE

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Keywords: e-infrastructure, research infrastructures, research data, data analysis.

INTRODUCTION

The team based at CSC – IT Center for Science Ltd. is a part of the ATM Center of Excellence with the purpose of developing, providing and supporting e-infrastructure services for the researchers in the CoE. The expertise in the team includes for example processing environments, research data services, scientific software, and expertise. CSC is the Finnish center of expertise in ICT providing services for research, education, culture, public administration and enterprises. CSC is a non-profit limited company owned by Finnish state and Finnish universities.

CSC is involved in key roles of several European e-infrastructure and research infrastructure projects. CSC coordinates the European Collaborative Data Infrastructure EUDAT and the associated H2020 project. CSC is coordinator of the Research Data Alliance European projects. It has close connections to e-infrastructure providers globally and represents Finland in key e-Infrastructure development projects such as EGI and PRACE, and is involved in several thematic high-level H2020 projects, such as ENVRIplus – collaboration of European environmental and earth system research infrastructures.

The activities of the group in the ATM CoE have focused on providing on-site support and training, improving efficiency of scientific software, developing the e-infrastructure resources and improving data availability. Main results of the mentioned topics will be provided in the following sections. The collaboration between IT infrastructure experts and researchers has covered several other topics ranging from providing expertise in visualization of research results to collaboration in international research initiatives. The latter are discussed in the impacts section, and this abstract also presents a brief outlook on next steps and future targets.

ACTIVITIES

Support on using the data and computing environment

The team has provided support on various aspects of utilizing the available e-infrastructure resources, including efficient use of supercomputers hosted by CSC, measurement and simulation data management as well as installation and use of scientific software. This activity includes an on-site support person for the Kumpula campus, Dr. Juha Lento, who gives direct support and is a contact person for additional questions. Important part of this support is also delivering training for the researchers and students.

In-depth support has been given at least for the following groups and topics: micro-meteorology models, climate models, atmospheric chemistry and physics, earth system modeling, and dynamical meteorology.

Development of the e-infrastructure resources

In collaboration with ATM CoE and the INAR national research infrastructure, CSC has acquired additional hardware in 2015 and 2016 to enable research on the field. The first purchase acquired additional nodes to the Taito supercluster. These have been used for climate modeling and re-analysis of climate data. The second installation was dedicated storage servers for the Pouta cloud platform. These are aimed for storing and distributing simulation results from earth system modeling that are part of the CMIP-6 experiment.
Improving data availability

Improving data availability is an important target of research infrastructures, also in the field of atmospheric science. CSC team’s work has been supporting this through two main actions: development and provision of Smart SMEAR portal for working with measurement data, and tools for distributing simulation data.

The SmartSMEAR is a web portal (https://avaa.tdata.fi/web/smart/smear/) that allows real time viewing of several measurements from SMEAR stations. The portal can be used for searching and viewing wide range of variables from different SMEAR stations (including Värriö, Hyytiälä, Helsinki and Puijo). Once the user finds the data sets of interest she can download them for further processing. There is also possibility to download data sets without first viewing them online, allowing advanced users to do downloads quickly. The portal even offers machine readable APIs to data and metadata.

The SmartSMEAR portal has been especially widely used at training courses and winter schools, where it provides an easy to use interface for students to access measurement data. Recent work on the portal has focused on usability and performance improvements.

Distribution of simulation data is an important part of Finnish participation to the IPCC global climate modeling experiment, the CMIP-6. The method to distribute the simulation results is the Earth System Grid Facility (ESGF), which is a federation of nodes each hosting and serving data for end users. ATM CoE will participate in the CMIP-6 with ESM simulations, and the corresponding ESGF node is planned to be implemented at CSC Pouta cloud platform with support from CSC experts.

FUTURE TARGETS

One of the key targets for next year is to deployment of the ESGF node, which will allow full-scale participation to global CMIP-6 collaboration. In addition to this, CSC will strive to keep the IT services for science on international top level both for the needs for ATM research and in general for all science fields. It is the long-term target of CSC’s participation in the Center of Excellence to bring e-infrastructure as an integral part of the research process. This includes both availability of services and ease of access for end-users, and support for research infrastructures such as the SMEAR measurement stations.

IMPACT OF THE WORK

State-of-the-art computational resources, data management systems and research environment in general facilitate efficient research. More and more research is depending on large data sets, ability to do data analytics efficiently, and sharing of research results. In this modern landscape the e-infrastructures are a key enabler. Moreover, it is reasonable to divide the work in a way that allows researchers to concentrate on their subject and let experts from IT field to take care of those services.

More effective use of available resources, such as computing systems, allows performing larger amount and more accurate calculations, thus speeding up the generation of results. On the other hand, this allows testing novel research hypothesis that require more effective computing.

The joint work of IT center and research groups has been active also towards international collaborations. There are, for example, several Nordic projects in which CSC and sites of research of ATM have jointly participated (including eSTICC and CRAICC). CSC is highly active in European e-infrastructure initiatives, coordinating the EUDAT Data Infrastructure, and being partner in European Grid Infrastructure EGI, Partnership for Advanced Computing in Europe (PRACE), the European Open Science Cloud project (EOSCpilot), and the forthcoming operational implementation project EOSC-hub. Combining this expertise with top research quality of the CoE is a fruitful start of joint activities internationally. This has been demonstrated in, for example, the H2020 ENVRI and ENVRI Plus projects.
The international work aims to strengthen the position of Finnish research groups internationally, facilitating access to research data resources globally, improving interoperability of data services, and overall improving exchange of ideas between researchers in different areas of the world.

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INTEGRATED ATMOSPHERIC AND EARTH SYSTEM SCIENCE RESEARCH INFRASTRUCTURE - ECOSYSTEMS

INAR RI Ecosystems

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INTRODUCTION

INAR RI Ecosystems is the ecosystem part of Integrated Atmospheric and Earth System Science Research Infrastructure, INAR RI, focusing on terrestrial ecosystem and biodiversity research. It is a research infrastructure project (2017-2021) funded by the Academy of Finland and the host organisations, and extends the INAR RI to cover ecological infrastructures in forests, peatlands, agricultural fields and catchment areas in subarctic, boreal and urban/agro-ecosystems. The purpose of INAR RI Ecosystem is to enable and support the Finnish ecosystem research and strengthen its linkages to atmospheric sciences. To do so, it will upgrade research infrastructures at various ecosystem observation stations and experimental stations and laboratories (Fig 1), coordinate their national activities and create deeper co-operation between them as well as between ecosystem researchers in Finland. It will also develop compliant, open data systems for research, education and the wider public. By doing this, INAR RI Ecosystems will provide extended understanding on the functioning of forest, peatland, agricultural, urban and lake ecosystems, and their interactions with the atmosphere.
ACTORS AND ACTIVITIES

INAR RI Ecosystems includes the Finnish contribution to eLTER RI (Integrated European Long-term ecosystem, critical zone and socio-ecological system research infrastructure) and AnaEE (Infrastructure for Analysis and Experimentation on Ecosystems). All the main actors on the environmental research in Finland are involved in INAR RI Ecosystems. The partner organizations include five universities: University of Helsinki (UH), University of Eastern Finland (UEF), University of Oulu (UO), University of Turku (UT) and University of Jyväskylä (JyU), and three national research institutes: Finnish Environment institute (SYKE), Natural Resources institute Finland (Luke), and Finnish Meteorological institute (FMI). In addition, the IT Center for Science (CSC) provides tools and methods for data analysis and management for all partners. The stations and sites of these institutes cover all major terrestrial and inland ecosystems in Finland.

INAR RI Ecosystems has a multidisciplinary approach to environmental research, and uses both experimental and observational methods. INAR RI Ecosystems operations are constructed from three complementary main pillars:

i) high-standard, long-term observation stations in different ecosystems for a baseline understanding, and for distinguishing short-term variability from long-term trends (all partners);
ii) experimental field sites and laboratory experiments to gain mechanistic understanding of ecosystem processes and interactions in changing climate (UH, UEF, LUKE, the Finnish Research Station network RESTAT);
iii) metadata service dedicated for the ecosystem research community to ensure compliant, open and easy accessibility of ecosystem-related data for scientific and monitoring purposes (all partners).

INAR RI Ecosystems field and laboratory facilities will develop high quality, integrated services for a variety of user groups and communities. INAR RI Ecosystems services include high level research infrastructures on ecosystem functioning and their responses to different pressures, and on energy and material fluxes within various ecosystems and between biosphere and atmosphere, access to both historical and currently produced ecosystem datasets, physical access to the highly equipped field sites and laboratories, scientific education, and method and technology transfer. INAR RI Ecosystems data is needed for enhanced understanding of ecosystem process and their interactions, for detecting long-term changes in environmental drivers and their impacts, for calibration/validation of remote sensing products, and for obtaining detailed process data for up-scaling to larger regions. The data and metadata will be open access and in an easily usable format.
INTERACTIONS AND EFFECTS

INAR RI Ecosystems activities will include interaction at several levels. The results and actions are widely discussed with a multidisciplinary research network as well as with research infrastructures also outside our own field (for example ICOS, ACTRIS) to gain expertise to better develop and co-create the ecosystem-focussed infrastructures (eLTER RI, AnaEE). The co-location of different RIs in the most instrumented sites, in addition creating possibilities for discussion and collaboration, will provide experiences in practical (technical, operational etc.) solutions that are tested and potentially can be implemented in a wider context, providing a benchmark for Europe in RI integration.

We also aim to collaborate with the spin-off companies to develop further the measurement equipment and to test prototypes. The high quality and wide array of INAR RI Ecosystems components allows active involvement of industry in testing equipment and methods, capacity-building and improved connections to a European-wide research community. This is already manifested in the involvement of a Finnish SME Masinotek in the eLTER H2020, where several INAR RI Ecosystems sites and organisations are partners. For example in AnaEE, the collaboration with industry is managed cost-efficiently centrally in all participating platforms by the AnaEE Technology Center.

The interaction with the civil society will be done for example through press releases (http://www.atm.helsinki.fi/FCoE) published approximately once a month reporting on new top level research results and projects, through educational publicly available material and tools (e.g. Climate.now, Open ilmastoporis, and Open IFS) and through popular articles. INAR RI Ecosystems also aims to interact with policy-makers especially in topics related to the climate change, use of natural resources and land-use. For example, the results from INAR RI Ecosystems are directly utilized in scientific argumentation in the debate on forest bioeconomy demonstrating the invaluable societal relevance of this research, and following the principle 'science-for-policy' (EASAC 2017). Also, important themes through the eLTSER platforms (two are currently active in INAR RI Ecosystems) are knowledge transfer and innovation in agriculture, forestry and rural areas; restoring, preserving and enhancing ecosystems related to agriculture and forestry; promoting resource efficiency and supporting the shift toward a low-carbon and climate-resilient economy in the agriculture, food and forestry sectors; promoting social inclusion, poverty reduction and economic development in rural areas.

INTEGRATION OF RESEARCH INFRASTRUCTURES

The ESFRI strategy report on research infrastructures (ESFRI 2016) recognized one core issue for future Environmental RI development being the demand to integrate on-going public agency monitoring programs with data collected for research purposes. INAR RI Ecosystems addresses this question. Finland has become one of the world leaders in this field at European and global level. Research on ecosystem sciences is closely linked to atmospheric research, especially regarding climate change and biogeochemical cycles’ topics. We have long and strong tradition on studying atmosphere-ecosystem interactions and feedbacks, and INAR RI Ecosystems is an integral part of this development (Fig. 2). One of the main impacts is promoting the integration of RIs in national and international settings, where INAR Ecosystems is one of the leading actors in Europe. INAR RI Ecosystems is the first and vital step towards a national Integrated Ecosystem Research Infrastructure. The INAR RI Ecosystems community is a bottom-up initiative to improve the national integration, and paves the way for the Finnish ecosystem research to actively participate in developing the integration between ICOS, AnaEE and eLTER RIs, together with leading European organisations, and embedded into the ENVRI plus concept. The Nordic ENVRI community is also providing a platform for collaboration among the ecosystem-specific RIs, and the possibilities for more efficient sharing of experiences in developing, implementing and operating RIs are being explored.
Figure 2. Illustration of European RIs I environmental research divided into thematic domains and their national representatives on Finnish roadmap. INAR RI Ecosystems is the initiative to construct a common national integrated RI for biosphere.

IMPACT

Sustainable use of natural resources and the state of environment and ecosystem services are in the core of INAR RI Ecosystems research agenda. INAR RI Ecosystems will provide invaluable information on current state of ecosystems and their plasticity to tolerate climate change. Understanding the functions of ecosystems will help to contribute to mitigating harmful changes, for example to accumulating a large part of anthropogenic carbon emissions. INAR RI Ecosystems will help to quantify the ecosystem services offered by different ecosystems and thus help to estimate their value in the economic sense and better involve the role of environment for example into the regional planning.

The socio-economic impacts of INAR RI Ecosystems through policy-making processes are strong. Long-term ecosystem studies have a significant impact and capacity to inform policy making concerning environmental issues for example through setting topics on the agenda, developing and selecting policy alternatives, developing opinion and argumentation by stakeholder groups and monitoring and evaluating progress (Hogan, 2005; UNICEF, 2008). INAR RI Ecosystem research results can support the development of new policies and more likely lead to adjustments of policies and increase policies’ effectiveness and efficiency. Thus, INAR RI Ecosystems will help to design cost-effective policy instruments and financial mechanism to reach agreed political targets (Research Councils UK, 2014; European Science Foundation; Daily et al., 2009).

INAR RI Ecosystems will offer answers to the grand challenges, such as biodiversity loss, climate change and deteriorating state of ecosystems through a comprehensive, coordinated and high-quality set of environmental and ecosystem research. Studying environment from a multi-disciplinary perspective and utilizing both experimental and observational approach allows us to do environmental monitoring, modelling, forecasting and impact analysis. This holistic, fundamentally multidisciplinary and integrated research strategy offers tools for better understanding the function of the environments and possibilities for mitigation, which are crucial for policy makers and public service designers.

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LABORATORY AND FIELD STUDIES ON REACTIONS, SAMPLING AND ANALYSIS OF GASEOUS COMPOUNDS AND PARTICULATE MATTER INCLUDING BIOAEROSOLS


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Keywords: Reaction experiments, solid phase microextraction Arrow, monoterpenes, bioaerosols.

INTRODUCTION

Biogenic volatile organic compounds (BVOCs) with different size, physicochemical properties and metabolic origin are emitted to the air by the biosphere (Peñuelas and Staudt, 2010). Some of these compounds take part in reactions in the atmosphere. For example, oxidation products of monoterpenes can participate in the formation of secondary organic aerosols (e.g. Riipinen et al., 2012). Other organic volatiles, like aldehydes, can also participate in atmospheric photolytic reactions and be involved in new particle formation processes (Hellén et al., 2004).

Amines are volatile, highly reactive and widely present in the atmosphere (Ge et al., 2011). The most abundant amines in the atmosphere are methylamine, dimethylamine, and trimethylamine. Recently, formation of nitrogen-containing low volatile compounds in reactions between pinonaldehyde and dimethylamine have been reported (Duporté et al., 2016), indicating the importance of amines in the aerosol formation in the atmosphere.

Pollen, fungal spores, bacteria, viruses and cell fragments of plants and animals are examples of bioaerosols emitted to the atmosphere (Després et al., 2007). Their importance to atmospheric chemistry and physics has created an increased interest towards their reliable determination. They are also considered to be a major source of proteinaceous materials in the atmosphere (Matos et al., 2016). It is proposed that proteins are degraded via enzymatic hydrolysis or thermal or photochemical decomposition into peptides or free amino acids. Amino acids can then serve as markers for bioaerosols.

METHODS

Flow tube reactor experiments for the ozonolysis of α-pinene in the presence or absence of dimethylamine (DMA) was performed in a borosilicate glass flow tube reactor (205 cm long, 4.7 cm i.d.). Purified dry air at atmospheric pressure and room temperature was used in the flow tube under laminar flow conditions. The total gas flow was 4.5 L/min resulting in a residence time of 53 s. Gas-phase products were analysed by high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) equipped with iodide reagent ion chemistry. Aerosol size distribution was measured with a differential mobility particle sizer (DMPS). In addition, gas- and particle-phase samples collected from flow tube experiments were analyzed by ultrahigh-performance liquid chromatography coupled to electrospray ionization orbitrap mass spectrometry (UHPLC–HRMS). Aerosol samples (PM1) were also collected from the SMEAR II boreal forest site at Hyytiälä, Finland during May–June of 2016 to confirm the flow tube reaction product chemistry at real atmospheric conditions. Additional quantum chemistry calculations were done for the clarification of enamine formation from pinonaldehyde and dimethylamine (Duporté et al., 2017).

Measurement of BVOCs from soil chambers was performed by SPME fiber sampling (PDMS/DVB fibers) and portable gas chromatography-mass spectrometry (GC-MS). Air samples were collected simultaneously by dynamic SPME to compare the type and relative amounts of BVOCs found in soil.
chamber samples with those measured in ambient air. The results obtained from the soil chambers were compared with BVOCs fluxes measured by PTR-QMS. In addition, effect of meteorological parameters on the results was clarified (Barreira et al., 2017a).

SPME Arrow sampling was tested for the collection of BVOCs from boreal forest ambient air. This novel SPME-based system consists of a steel rod coated with a larger amount of sorbent material compared to that in the traditional SPME fibers, offering increased capacity but maintaining the compatibility for desorption and analysis in a conventional GC-MS (Helin et al., 2015). The coated rod can be withdrawn inside a steel tube, making the device very robust. For comparison, samples were collected simultaneously also by SPME fibers. The effects of meteorological parameters on the measured amounts of BVOCs were evaluated. The characteristics of SPME Arrow coating materials used in this work (polydimethylsiloxane/divinylbenzene (PDMS/DVB) and PDMS/Carbon WR) were studied in the laboratory before the field campaign. Also, static and dynamic SPME Arrow collection modes were compared. (Barreira et al., 2017b)

In bioaerosol study, size-segregated aerosol samples were collected in boreal forest during one year period. Aerosol samples were analysed for DNA concentration, microorganism-DNA (bacteria, Pseudomonas and fungi) and free amino acids (FAAs). The annual concentration and size distribution variation of microorganisms and FAAs were investigated in detail in order to understand their potential sources. Impactor was used for the sampling of four particle size fractions (<1.0, 1-2.5, 2.5-10 and >10 µm) below the canopy. The sampling flow rate was on average 30 L/min and the collection time varied from one to four days (sampling volume 76-144 m³). After ultrasonic assisted extraction, free amino acids were determined by liquid chromatography-tandem mass spectrometry. Commercial DNA extraction kit with slight modification was used. The DNA concentration and purity were measured spectrophotometrically at 260 nm and 280 nm with NanoDrop ND-1000. The DNA samples were stored at -20 °C prior to qPCR determination of bacterial and fungal DNA amounts. (Helin et al., 2017)

CONCLUSIONS

For α-pinene ozonolysis, flow-tube reactor experiments revealed the enhancement in new particle formation and secondary organic aerosol formation in presence of dimethyl amine. Both particle number and size were increased in presence of DMA (Figure 1). Various nitrogen containing compounds were seen in the analysis of gas and particle-phase reaction products using high-resolution mass spectrometry. Decrease of the signals from the ions attributed to pinonic (m/z 311, C_{10}H_{16}O_3I^-), pinic (m/z 313 C_{9}H_{14}O_4I^-), and hydroxy-pinonic acids (m/z 327, C_{10}H_{16}O_4I^-) were observed after the injection of DMA into the flow tube. Water molecule that lowered the activation energy of the reaction between pinonaldehyde and DMA by 10 kcal/mol activated some of the reactions and formation of N-containing reaction products to occur most probably on the surface of the molecular cluster or aerosol. Some of these reaction products were also observed in atmospheric aerosols collected at the SMEAR II Station (Hyytiälä, Finland).
Figure 1. Changes in particle number and diameter during the flow tube reactor experiments in $\alpha$-pinene ozonolysis with and without DMA.

The most abundant BVOCs measured in soil chambers and ambient air were $\alpha$-pinene and $\Delta^3$-carene (these species constituted 80-90% of the measured monoterpenes) and their relative concentrations were similar in different chambers. In addition to differences in vegetation, higher humidity of chambers 13 and 15 presumably increased the surface losses of terpenes and aldehydes, giving explanations to the higher concentration levels in chamber 10 (Figure 2). Amounts of aliphatic aldehydes were relatively lower in soil chambers than in ambient air.

Figure 2. Comparison between the amounts of monoterpenes (A) and aldehydes (B) measured in different soil chambers and in ambient air by SPME-GC-MS.

Arrow sampling system was for the first time used for the static and dynamic collection of BVOCs from the boreal forest, and samples were subsequently analyzed on-site by gas chromatography-mass spectrometry (GC-MS). A significant improvement on sampling capacity was observed with the new SPME Arrow system when compared to SPME fibers, with collected amounts approximately two times higher for monoterpenes and 7-8 times higher for aldehydes (Figure 3). BVOC species exhibited different affinities for the type of sorbent materials used (PDMS/Carbon WR vs. PDMS/DVB). Higher collection efficiency was obtained in the laboratory with the dynamic SPME Arrow sampling system compared to static mode. However, in the field sampling this difference was much smaller.
Figure 3. Comparison between the mass of identified monoterpenes (A) and aldehydes (B) collected with different PDMS/DVB SPME devices (fiber and Arrow) from ambient air and measured by GC-MS.

Elevated levels for FAAs and bacteria were observed during the pollen season in SMEAR II Station, whereas the highest abundances for fungi were observed in autumn (Figures 4 and 5). According to our results, during the spring pollen season even up to ~77% of total PM may be of biological origin. During late summer and autumn, bioaerosols were accumulated in the size fraction of 2.5-10 µm. In autumn, the relative amount of biomass in PM was estimated to be around ~10%.

Figure 4. Amount of free amino acids (FAA) in different size aerosol samples collected in SMEAR II station in Hyytiälä during the year 2014.
Figure 5. Amount of bacteria and fungi in different size aerosol samples collected in SMEAR II Station in Hyytiälä during the year 2014.

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INTRODUCTION

Weather affects almost everyones’ lives. The majority of time, for most people, although the weather may be inconvenient, it does not lead to severe consequences such as injury, death and major economical loss. However, occasionally, high-impact weather events do occur. For example, severe thunderstorms can lead to heavy precipitation and flooding or a particularly intense mid-latitude, synoptic-scale storm can cause high winds which damage infrastructure, buildings and disrupt travel. Therefore, to enable society to prepare and reduce exposure to such high-impact weather, accurate weather forecasts are required. However, in addition, our climate is changing and the frequency, intensity and location of extreme, high-impact weather events in the future is very likely to change. Therefore, to enable policy makers to plan ahead, it is also vital to predict with confidence how such extreme weather events will change in the future. The overall aims of the dynamic meteorology group are to:

1. Develop in-depth physical understanding of meteorological phenomena, such as deep convection and high impact extra-tropical storms, and apply this knowledge to improve numerical weather prediction models and hence weather forecasts.

2. Develop ensemble prediction and algorithmic parameter estimation techniques together with open source software packages to permit further improvement of numerical weather forecast models.

3. Quantify how weather patterns and the hydrological cycle will change in the future.

4. Understand the interactions between atmospheric aerosols, radiation, microphysical processes and the large-scale circulation.

5. Assess the accuracy of the current generation of coupled climate models, understand inter-model variations and factors that affect regional temperature changes.

Currently there is a wide range of on-going research topics in the dynamic meteorology group which cover both weather and climate time-scales. Our research group uses a range of numerical models and large data sets (e.g. reanalysis data and CMIP5 model output). Therefore, many of our activities are reliant on computing resources and the support of CSC – IT Center for Science. Our group has developed an excellent and highly beneficial working relationship with the division’s application specialist from CSC - Juha Lento. Below a short introduction is given to our on-going projects.
PHYSICS OF DEEP CONVECTION

Atmospheric deep convection is the mechanism behind showers of rain and many severe weather phenomena, such as thunderstorms, hurricanes, tornadoes and flash floods. The processes controlling the physics of deep convection need to be understood and parameterized in order to produce accurate weather forecasts and climate predictions. In our group, we study the fundamental, yet not properly understood, relationship between deep convection and lower tropospheric humidity. The mechanism behind this relationship has been studied extensively, yet models still struggle to represent it accurately.

In the first part of this project, an analysis of sounding and precipitation data was conducted. A new mechanism to explain the relationship between deep convection and lower tropospheric humidity was found. More specifically, after precipitation over dry areas robust lower tropospheric warm anomalies were observed, whereas over moist areas these warm anomalies were absent. Our results suggest that the warm anomalies may be the result of subsidence below a layer of strong evaporation of precipitation. As lower tropospheric warm anomalies are known to inhibit deep convection, we believe that evaporation of precipitation is a key mechanism in controlling the formation of future deep convection and should be accounted for in both models and theories of convective phenomena (see Virman et. al. in this issue for more information).

AEROSOL EFFECT ON DEEP CONVECTIVE CLOUDS AND UPPER TROPOSPHERIC HUMIDITY

Aerosol-cloud interactions are the largest source of uncertainty in the current radiative forcing estimates of the global climate. Especially processes related to deep convective clouds are poorly understood. Aerosol-induced suppression of precipitation in the updrafts of deep clouds can transport more water into the upper troposphere. Even without changes in the total amount of precipitation, changes in cloud microphysics, namely sublimation of the increased amount of hydrometeors in the upper troposphere, can increase the upper tropospheric humidity (UTH). As radiative transfer is highly sensitive to UTH, this means aerosols may have a less negative radiative forcing on climate than currently taken into account in the estimates of anthropogenic climate change.

In a recent study (Riuttanen et al., 2016) we used satellite data from June, July and August in the years 2007-2013. The China outflow region (25-45°N, 120-149°E) was chosen for a more detailed study. UTH, i.e. the relative humidity with respect to water, in a layer between approximately 200 and 500 hPa, was obtained from the microwave humidity sounder (MHS) on board the MetOp-A satellite. We used AOD from the Moderate Resolution Imaging Spectroradiometer (MODIS) instrument on board the Terra satellite and the daily rainfall product, 3B42, from the Tropical Rainfall Measuring Mission (TRMM) multi-satellite analysis. The UTH data were binned according to daily precipitation in the same 1x1 degree grid and only cases when the daily precipitation exceeded 1 mm were considered. The sensitivity of the radiative transfer to perturbations in the UTH was tested by using the libRadtran radiative transfer code.

Higher values of UTH were observed in association with high AOD for cases with similar amount of precipitation. AOD was observed to increase almost linearly as a function of cirrus fraction. Therefore linear regression was applied to AOD data in order to remove any possible data contamination by cirrus. Considerable efforts were made to study the effect of meteorological covariation or other possible causes behind the observations, for example by using ERA Interim reanalysis data. We conclude that any other causes but aerosols behind the increase in UTH are very unlikely.
ENSEMBLE PREDICTION AND PARAMETER ESTIMATION

Ensemble predictions (ENS) in meteorology are operationally applied to assess the day-to-day uncertainties of weather predictions, or "predict the predictability". These uncertainties are due to unavoidable small errors in the initial state and the model formulation. Over the past five or so years, our group has pioneered the use of ENS to assess uncertainties in model closure parameters. All geophysical prediction models contain such parameters and a handful of them are critically important for the forecast quality (Berner et al., 2017). To this end, we have developed algorithmic parameter estimation techniques, foremost the ensemble prediction and parameter estimation system (EPPES), which has proven to shift the effort of model tuning from the domain of human learning to the domain of expert assisted machine learning. In academia, running ensemble predictions is tedious due to the huge number of simulations needed to gauge the small but highly non-linear model parameter space. A recent innovation from our group is a software package called OpenEPS, which facilitates administration of the model runs, output file post-processing, and parameter estimation, and opens new opportunities to apply ENS outside operational centres.

CLIMATE CHANGE AND EXTRA-TROPICAL CYCLONES

Two complementary approaches are taken to determine how the structure of extra-tropical cyclones will change in the future. Both approaches are based on idealized pseudo climate change experiments conducted with atmosphere only numerical models. Such experiments are easier to interpret and understand than simulations created using complex Earth System models.

In one study, the sensitivity of one idealised weather system (baroclinic wave) to environmental temperature changes is examined with the Weather Research and Forecast (WRF) model. The temperature forcings applied in 10-day long model experiments are similar to what are expected in a warmer climate: 1) uniform temperature increase, 2) decreased lower level meridional temperature gradient and 3) increased upper level meridional temperature gradient. Preliminary results suggest that the dynamics of extra-tropical cyclones are most sensitive to changes in the lower-tropospheric temperature gradient while changes to the upper-tropospheric temperature gradient play a smaller role. The results also show that uniform increases in temperature enhance diabatic processes and result in deeper cyclones but that changes to dynamical properties of the cyclones, for example, kinetic energy, are rather modest. (see Rantanen et. al. in this issue for more information).

In the second study, the response of the climatology, characteristics and structure of extra-tropical cyclones to climate change are investigated by performing 10-year long aqua-planet experiments with OpenIFS. Two experiments were performed: a control simulation and a simulation where the sea surface temperatures were uniformly increased everywhere by 4 K. The large-scale circulation response to this warming is similar to that found in CMIP5 models; a poleward shift of the jet streams and storms tracks. The most intense extra-tropical cyclones have stronger winds and more intense precipitation associated with them in the warmer climate. (see Sinclair et. al. in this issue for more information).

HYDROLOGICAL CYCLE UNDER CLIMATE CHANGE

Climate change will lead to increases in atmospheric water vapour content and changes in precipitation patterns which will impact the hydrological cycle. One aspect of the hydrological cycle is river discharge which can be simulated using a hydrological model. Hydrological models require as input estimates of precipitation and temperature and, for climate change predictions, these come from either global (GCMs) or regional (RCMs) climate models. However, GCMs and RCMs have biases which must be corrected for before they can be used as forcing in hydrological modeling stud-
ies. A group of statistical tools designed for this purpose are the so-called model output statistics (MOS). These methods vary in complexity from simple scaling of the time-mean climate to more sophisticated methods which account for biases in the daily variability. Some of the more complex methods also take different types of correlation (e.g., inter-variable) structures into account in their adjustments. These methods are routinely applied in many climate change impact studies but their performance in the changing climate is not well known.

Our first objective was to identify which methods perform well when constructing bias adjusted projections for future climate, not only from the climate modeling, but also from the hydrological modeling, perspective. In addition to the independent bias adjustment of temperature and precipitation, more complex multivariate methods, which aim to take biases in the inter-variable correlations between temperature and precipitation into account, were tested. All the required hydrological simulations were made with the European scale application of the Hydrological Predictions for the Environment (HYPE) model developed in SMHI. We concluded that it is practically impossible to identify a single universally well performing method, meaning that several well-performing methods should be used in parallel both for temperature and precipitation. Furthermore, although one could expect that improving inter-variable correlations between temperature and precipitation would improve the simulation of hydrological processes sensitive to co-variations in them (e.g., snow melting and accumulation around the melting point), the benefit gained by using complex multivariate methods is rather modest, although the simulation of some hydrological aspects is somewhat improved.

Our second objective was to put the inherent uncertainties related to the choice of the MOS method into the same context as the GCM-RCM uncertainties. GCM-RCM uncertainties were found to dominate both for temperature and precipitation, although MOS method uncertainties are non-negligible, especially in terms of precipitation and the extremes in the tails of the distributions. Similar conclusions hold for changes in river discharges in the Scandinavian region. (See Räty et. al. in this issue for more information)

**ENERGETICS OF CLIMATE CHANGE AND CLIMATE VARIABILITY**

Energetics is in the core of climate change and climate variability. For example, an increase in greenhouse gases reduces the long-wave radiation escaping to space. To balance this decrease, the surface and the lower atmosphere must radiate more which requires an increase in the global mean temperature. However, the magnitude of the response is modulated by feedbacks associated with changes in (e.g.) water vapour, clouds and surface albedo that either amplify or reduce the original imbalance. In addition, the net energy flux from the atmosphere to the surface moderates the warming before the new equilibrium is reached. At sub-global scales, changes in atmospheric and oceanic energy transport also play an important role.

To understand the factors that affect regional temperature changes in global climate models, we have developed a method that allows one to decompose the model-simulated changes to contributions of six main factors: changes in the clear-sky greenhouse effect, surface albedo, atmospheric clear-sky radiative properties for solar radiation, clouds, atmospheric energy flux convergence, and the net surface heat flux (Räisänen, 2017). An application of this method to CO₂-induced temperature change in CMIP5 models shows that the multimodel global mean warming is dominated by the enhanced clear-sky greenhouse effect, but other components of the energy balance substantially modify the geographical and seasonal patterns of the change. For example, changes in the net surface energy flux are crucial for the muted warming over the northern North Atlantic and for the seasonal cycle of warming over the Arctic Ocean. The three most important terms for intermodel differences in warming are the changes in the clear-sky greenhouse effect, clouds, and the net surface energy flux, making the largest contribution to the standard deviation of annual mean temperature.
change in 34%, 29% and 20% of the world, respectively.

The same energetic principles also apply to interannual temperature variability, which is crucial, for example, for its connection to prolonged heat waves and cold periods. Using the ERA-Interim and MERRA2 reanalyses, our ongoing work has started to reveal the energetic origins of this variability. Over the oceans, a duality emerges between net-surface-flux-dominated variability in the tropics and atmospheric-energy-flux-convergence-dominated variability at extratropical latitudes. Variations in atmospheric energy flux convergence also tend to drive the temperature variability over the extratropical continents in winter, but in summer cloud variations take the leading role. (see Räisänen in this issue for more information).

SOLAR RADIATION, AEROSOLS AND CLOUD PARTICLES

Solar radiation is the main source of energy for the Earth-atmosphere system. The uneven distribution of incoming solar radiation drives the atmospheric circulation and thereby weather and climate. In order to describe the interactions of the atmosphere with radiation, it is essential that its composition, including aerosols and cloud particles, is known. These interactions depend both on the properties of the radiation (wavelength and polarization) and particles (size, shape, and composition). This project concentrated on common particle types that have nonspherical shapes: ice crystals and mineral dust. If these particles were assumed to be spherical, their radiative effects would be erroneously estimated. However, this simplification is widely used since the lack of exact, analytical solutions makes it very challenging to account for the nonspherical shapes realistically.

Modelling the radiative effects of atmospheric particles includes several challenging stages where approximations cannot be avoided. However, it is essential to avoid unnecessary simplifications where those are known to produce considerable errors in the results. Recent computational and methodological advances in light scattering and radiative transfer have made possible the use of more morphologically faithful particle shape models in atmospheric radiation research, and Haapanala et al. in this issue demonstrate these advances all the way from single-particle scattering computations to radiative effects and even global climate models.

INTERACTION AND ON-GOING COLLABORATIONS

The dynamic meteorology group has many strong on-going collaborations, both within the Centre of Excellence, at national and international level. Main collaborations and activities include:

WITHIN THE CENTER OF EXCELLENCE:

- **Himalayan Aerosol factory**: This is a project led by Federico Bianchi, Atmospheric Mass Spectrometry Group. The aim was to determine if new particle formation takes place at high altitude in the Himalaya and whether particles observed in high altitude Himalayan valleys can be efficiently transported to the free troposphere. The dynamic meteorology group contributed to this project by performing high resolution simulations with WRF and FLEXPART (a Lagrangian dispersion model).

ON A NATIONAL LEVEL:

- **Finnish Meteorological Institute (FMI)**: We have numerous collaborations with researchers in FMI and many of the senior members of staff in our group also act as Ph.D supervisors for those employed by FMI but enrolled in our doctoral program.
• University of Lappeenranta: The main reason for this collaboration between our group and Professor Heikki Haario’s group in Lappeenranta is the co-development of the algorithmic parameter estimation techniques and ensemble prediction methods.

INTERNATIONALLY:

• European Centre for Medium Range Weather Forecasts (ECMWF): The main collaboration concerns OpenIFS. Our group has been one of the first groups to extensively use OpenIFS in teaching and research. Our research with OpenIFS, particularly in term of the ensemble prediction system and parameter estimation work is conducted in close collaboration with ECMWF and the results will feedback onto the operational model development at ECMWF. In addition, the development of the aqua-planet version of OpenIFS was done in collaboration between ECMWF and the University of Helsinki.

• COST Action: Our group actively participated in the EU-funded COST Action ES1102 VALUE (2012-2015), where a large number of different types of bias adjustment methods together with other statistical methods have been inter-compared within the VALUE framework. Results from the first framework studies have been mostly completed and will be published in a special issue in International Journal of Climatology.

• Swedish Meteorological and Hydrological Institute (SMHI): Our group has collaborated with SMHI in the use and development of the hydrological model HYPE as well as its application in climate change impact studies.

FUTURE OUTLOOK

Future plans include:

• Continue the development and use of OpenIFS in both teaching and research.

• More efficiently exploit links between weather and climate by utilizing our model hierarchy of OpenIFS and EC-Earth (OpenIFS is the atmospheric model of EC-Earth).

• Understand the energetic origin of temperature extremes and future changes in temperature variability

• Continue to improve our interaction and collaboration with other groups in the center of excellence.

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ATMOSPHERIC MASS SPECTROMETRY: RECENT PROGRESS

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Keywords: MASS SPECTROMETRY, CLUSTERS, HOM, AEROSOL FORMATION.

INTRODUCTION AND RECENT BREAKTHROUGHS

Research at the Atmospheric Mass Spectrometry research group has focused on understanding the formation of secondary aerosol precursors, production of clusters, early steps of new particle growth from cluster sizes toward climatically relevant sizes of cloud condensation nuclei, and secondary organic aerosol mass production. We also aim at an interdisciplinary approach by connecting our observations to, for example, biological and other environmental variables.

The recent breakthroughs include:

1) We made a study in Antarctica during 2014-2015 summer season and, after detailed analysis of the data, we have now revealed the exact molecular steps, including the chemical species involved in cluster and new particle formation. The results will be reported later.

2) During our more recent campaign in the Arctic – Ny Ålesund Svalbard 2017, together with CNR Italy – we discovered secondary cluster formation mechanisms and chemical species involved. We also resolved the growth mechanisms of secondary aerosol to climatically relevant sizes. Combined with the wide range of environmental and biological variables recorded by other groups at the site, we believe we can demonstrate the whole chain from biological activity to cloud condensation nuclei formation. Naturally, also these results need first to be published in a peer reviewed journal, and no details are yet reported here.

3) As a side product of our atmospheric research, and especially that related to instrument development, we found means for extremely sensitive explosive trace detection (ETD). Lowest detection limits for, e.g., hexogen and TNT vapours below 1 part per quadrillion was achieved. ETD is of great interest due to the present day threats related to international terrorism and there is high commercial potential associated with novel technologies. Building on our initial findings and subsequent, fairly large research efforts, a new commercial spin-off company, Karsa Ltd., was established in 2016.

4) Experiments performed in the CLOUD chamber in CERN showed that highly oxidized multifunctional organic compounds (HOM) from alpha-pinene oxidation under atmospherically relevant conditions can form clusters at rates potentially sufficient for this purely biogenic mechanism to have had a substantial contribution to new particle formation and growth in the preindustrial atmosphere (Kirkby et al., 2016, Nature, Tröstl et al., 2016, Nature). Further experiments were performed during CLOUD 11 campaign where we aimed to simulate new particle formation as recorded in boreal forest environment today, with anthropogenic influence due elevated SO₂ concentrations. Also these results will be reported later in a peer reviewed journal publication.

5) We reported the first identification HOM from aromatic precursors in a joint experimental-computational effort together with collaborators from Germany and China (Wang et al., 2017). Several different alkyl benzenes were studied, and the yields of HOM were theoretically predicted to increase with the size of the alkyl group, which was also verified by experiments.

6) Several types of pollution sources of organic aerosol at our SMEAR II site in Hyytiälä were identified using novel chemometric analysis methods based on aerosol mass spectrometer data.
(Äijälä et al., 2017). Some of the more surprising pollution types included large bursts of amines in the aerosol, primarily during winter months. The source of this aerosol remains the target of a subsequent study.

7) We made observations of evening time cluster formation in boreal forest (Rose et al., MS submitted, see also these proceedings) associated with production of biogenic vapours. These results provide insight into the pure biogenic particle formation we investigated in CLOUD – CERN (Kirkby et al., 2016)

ONGOING RESEARCH AND FUTURE GOALS

Current research topics include, but are not limited to, the following broad topics:

- Resolving the detailed molecular steps and relevance of different NPF mechanisms in polar and oceanic locations.
- Simulating marine and coastal iodine NPF in CLOUD chamber with the aim to reproduce our recent coastal and polar findings regarding NPF via sequential addition of iodic acid (HIO₃) (Sipilä et al., 2016, Nature).
- Resolving the precursors and formation mechanisms of iodic acid, HIO₃
- Comparison of NPF and associated chemistry in a variety of European environments via application of a mobile platform.
- Always ongoing, yet not achieved goal is to resolve the molecular steps of cluster formation in the highly complex boreal forest environment.
- Characterizing the importance of different oxidation pathways, primarily in the boreal regions but also elsewhere, of VOC to form condensable vapors. This includes identifying the roles of different oxidants, perturbations caused by NOₓ, and the role of temperature in the formation of HOM.
- Identifying the physical and chemical characteristics (volatility, reactivity, etc) of HOM that allow them to become incorporated into aerosol particles.
- Assessing the role of particle phase reactions in formation of SOA.

CONCLUSIONS

The research within the Atmospheric Mass Spectrometry group continues to yield high-impact scientific results. Especially year 2016 has shown to be an exceptional year when it comes to Nature and Science publications. Since that we have focused on collection of new data and are now, with several fresh breakthroughs in our hands and hard disks, looking forward to similar success within the next year or two.

Much of the ongoing and future work relate to improving our understanding of the mechanisms producing low-volatile vapors through gas phase reactions, and their subsequent contribution to NPF and SOA.

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Monomethylamine, dimethylamine, and trimethylamine (MMA, DMA, and TMA, respectively) have been shown to enhance sulfuric acid-driven particle formation more efficiently than ammonia. There is both experimental and theoretical evidence of differences between these amines in the potential formation of new particles. We studied cluster formation of MMA, DMA, and TMA with sulphuric acid, and conclude that formation of nanometer-sized particles together with sulphuric acid and its dependence on ambient conditions is roughly similar for DMA and TMA, while particle formation from sulfuric acid and MMA is weaker and significantly more sensitive to ambient conditions. Therefore, merging MMA together with DMA and TMA in particles formation schemes introduces inaccuracies in the formation rates (Olenius et al. 2017). As recent experimental evidence suggests also diamines as effective enhancers of sulphuric acid driven atmospheric new particle formation, we have investigated the molecular interactions between sulphuric acid and the diamine putrescine. Our results show that putrescine significantly enhances the formation of new particles compared to dimethylamine. (Elm et al. 2017b) Increasing interest in CO$_2$ capture technology may lead to emissions of monoethanolamine (MEA) into the atmosphere. We have studied clustering of sulphuric acid with MEA, showing that the enhancing potential of MEA is less than that of dimethylamine (DMA), but much greater than methylamine (MA), in contrast to the order suggested solely by their basicity (MEA < MA < DMA). The results imply that MEA released in the atmosphere could be removed by participation in H$_2$SO$_4$-based new particle formation. (Xie et al., 2017) These finding suggests that a large range of amines with different basicities can be involved in observed new particle formation events.

We have found that sulfuric acid clusters with pinic acid and even more strongly with MBTCA (3-methyl-1,2,3-butanetricarboxylic acid), an organic acid identified as one product of alpha-pinene oxidation. The growth of the smallest clusters is however limited, implying that other stabilizing vapours are required for new particle formation to be driven by these compounds (Elm et al. 2017a). We then proceeded to study whether their clustering in enhanced by the presence of a bisulphate anion HSO$_4^-$, an ammonium cation NH$_4^+$, or an ammonia NH$_3$ molecule. We conclude that it is unlikely that clustering of the studied organic acids and sulphuric acid, even together with bisulfate, ammonia, or ammonium can drive new-particle formation. Other mechanisms such as chemical reactions are needed to explain observed new-particle formation events in the presence of oxidized organic compounds resembling the acids studied here. (Myllys et al. 2017)

FATE OF CLUSTERS IN APi-TOF MASS SPECTROMETER

We have studied the fate of sulfuric acid clusters inside Atmospheric Pressure interface Time Of Flight mass spectrometer (APi-TOF). Combining a high resolution Differential Mobility Analyzer (DMA) with the APi-TOF allows us to measure the cluster size independently of the mass spectrometer, and separate
clusters based on their size. Sulfuric acid (H$_2$SO$_4$) clusters were produced by ElectroSpray Ionization, guided into the DMA where ((H$_2$SO$_4$)$_2$HSO$_4^-$) clusters were selected and injected into the mass spectrometer. We have observed that the clusters are strongly affected by the tuning of the API-TOF, and fragmentation of (H$_2$SO$_4$)$_2$HSO$_4^-$ into sulfuric acid dimer (H$_2$SO$_4$HSO$_4^-$) as well as monomer (H$_2$SO$_4$) is always observed. We are developing theoretical model to describe and predict the transformation processes of clusters inside the API-TOF.

THEORY AND SIMULATION METHOD DEVELOPMENT

We have shown how to correctly calculate free energies for atmospherically relevant complexes when multiple conformers and/or isomers are present, advising against usage of an erroneous formula in recent articles. If vibrational frequencies and thus Gibbs free energies of the individual conformers are unavailable, we recommend not to attempt to correct for the presence of multiple conformers and instead use only the global minimum conformers for both reactants and products. However, if the free energies for the conformers are calculated for both reactants and products, their effect can be accounted for by the statistical mechanical methods presented in this article (Partanen et al. 2016).

In Monte Carlo approaches to nucleation work of cluster formation is calculated by configurational sampling under fully isothermal conditions, and nucleation rate is deduced from this result. In molecular dynamic studies artificial thermostatting methods are used to control the temperature of the simulated system. We have compared the nucleation rates from molecular dynamic simulations to those from Monte Carlo simulations. The results reveal that none of the artificial thermostatting methods result in a fully isothermal behaviour, and realistic temperature control can only be achieved by using of a carrier gas as a thermostat.

ICE NUCLEATION

Experiments have revealed the ice nucleation activity of different types of compounds and highlighted the importance of surface irregularities. The molecular-scale processes responsible for ice nucleation are still not well known, and there are considerable challenges in atomic-scale characterization of complex, imperfect surfaces. Ice-like surface geometry has been suggested as key to effectiveness to act as ice nucleation seed. Our molecular dynamics simulations show that surface with a good lattice match with hexagonal ice nucleates ice effectively at the 10-100 nanosecond time scales attainable with simulations in immersion mode, which is considered the most important ice cloud formation process. Results from simplified monoatomic water potential simulations show that surface geometry alone can explain the high nucleation activity of AgI, whereas K-feldspar, believed to be one of the most important ice nucleation agents in the atmosphere, shows very weak activity in these simulations. Thus, the real surface chemistry and/or defects of the material must be modelled to capture its behaviour as ice nucleation seed.

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INTEGRATED CARBON OBSERVATION SYSTEM - ICOS-FINLAND AND ICOS-ERIC

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Keywords: Greenhouse gases, long term observations, climate change, distributed research infrastructure

BACKGROUND

Climate change is one of the most challenging problems mankind will have to cope with in the coming decades. The driving force of current and future climate change is the increase of greenhouse gas (GHG) concentrations in the atmosphere, driven by man-made emissions that overtake natural cycles of carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4}) and nitrous oxide (N\textsubscript{2}O). The concentrations of CO\textsubscript{2} and CH\textsubscript{4} in the atmosphere are at their highest in the past 25 million years. Current levels of CO\textsubscript{2} have increased by 30\% from pre-industrial times and they continue to rise, as fossil fuel emissions are climbing up. Current levels of CH\textsubscript{4} are nearly thrice the pre-industrial value.

The primary agents of change in GHG concentrations are fossil fuel combustion and modifications of global vegetation through land use change, in particular deforestation. The natural carbon cycle absorbs half of the anthropogenic emissions. At the current atmospheric level of CH\textsubscript{4}, the natural oxidizing power cleans up almost all the CH\textsubscript{4} injected by human and natural sources but expected increases of emissions will further raise the CH\textsubscript{4} mixing ratios.

Deeper understanding of the driving forces of climate change requires full quantification of the GHG sources and sinks and their dynamics. These can be assessed by long term, high precision observations in the atmosphere and at the ocean and land surface. ICOS will provide the long-term observations required to understand the present state and predict future behaviour of the global carbon cycle and GHG emissions.

We describe here also ICOS ERIC since it is the backbone of ICOS infrastructure and is in close collaboration with University of Helsinki and Finnish Meteorological Institute, although it is not formally a part of Center of Excellence.
ICOS-FINLAND

Currently more than 40 persons (technicians and researchers) are contributing to the operation of ICOS-Finland. ICOS-Finland is established by three national partners: University of Helsinki (UH), Finnish Meteorological Institute (FMI), and University of Eastern Finland (UEF). ICOS-Finland is operating 14 ICOS measurement stations: four Class 1 atmospheric, two Class 1 ecosystem, two Class 2 ecosystem and six associate ecosystem measurement sites. Atmospheric stations are tall towers or otherwise represent air masses above the surface layer. Ecosystem stations represent forest, wetland and lake ecosystems and urban environment. An important task of ICOS-Finland is to bring together researchers in GHG studies nationally. ICOS-Finland invites the national research community to discuss and present recent results in regular scientific meetings. ICOS-Finland national meetings were held in Hyytiälä on November 2010, in Utö on April 2012, in Kuopio in May 2014, and in Helsinki on October 2015. Since 2017, all the Nordic ICOS Networks organise the symposium jointly, and it is meant to take place every second year alternating with the ICOS Science Conference.

For the participation in the Atmospheric Thematic Centre (ATC), FMI is operating a mobile laboratory and a laboratory in Kumpula, which are needed for our Quality Control task of the European ICOS network. It has audited so far six Atmospheric stations in five countries.

ICOS-ERIC

ICOS Research Infrastructure is coordinated and integrated by the ICOS European Research Infrastructure Consortium (ERIC). ICOS ERIC was established by the decision of the European Commission in November 2015, with the statutory seat in Finland, and the ICOS Carbon Portal located in Sweden. ICOS is one of 13 currently existing ERICs.

ICOS ERIC holds a Landmark status in the European Strategy Forum on Research Infrastructures (ESFRI) Roadmap since March 2016. The ESFRI Roadmap identifies new Research Infrastructures (RI) of pan-European interest corresponding to the long-term needs of the European research communities, covering all scientific areas, regardless of possible location.

The second ICOS Science Conference was held in Helsinki in September 2016, with more than 250 participants from all around the world, giving huge visibility also to the ICOS Finland.

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MICROMETEOROLOGY, GREENHOUSE GASES AND BIOGEOCHEMICAL CYCLES
RESEARCH TEAM: OVERVIEW OF SCIENTIFIC ACTIVITIES


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Keywords: Turbulent fluxes, greenhouse gases, carbon cycle, water cycle, carbonyl sulphide, boreal forest, lake, peatland, eddy covariance, lake model

INTRODUCTION

The coupling of the Earth's surface and the overlying atmosphere through mass and energy fluxes has an important role in atmospheric chemistry and physics in addition to boundary layer meteorology and ecosystem research. Micrometeorology, Greenhouse gases and Biogeochemical cycles group of University of Helsinki aims at increasing the fundamental understanding of biosphere-atmosphere interactions in different ecosystems and to apply the gained information for practical applications and purposes. The group has a comprehensive experience on ecosystem scale flux measurements carried out by means of micrometeorological techniques. Long term and continuous measurements are performed over forest, peatland and freshwater ecosystems and in urban environment. The work is done in close co-operation with other FCoE research teams from University of Helsinki (Ecosystem processes, Soil Dynamics), from Finnish Meteorological Institute (Greenhouse gases), as well as with other national and international collaborators. In 2017 a new University of Helsinki project ATMATH started, which is strengthening collaboration between profs. Antti Kupiainen and Matti Lassas (both in Department of Mathematics and Statistics) and prof. Hanna Vehkamäki. We report below summaries of recent research studies and activities performed within the group.

METHODOLOGICAL ASPECTS AND DEVELOPMENTS

Advances in Eddy Covariance method

During last few years the research group has been actively involved in several activities related to greenhouse gas (GHG) measurement techniques, protocols and data harmonization within ICOS and other international projects. The work includes advances in the eddy covariance (EC) method for methane and nitrous oxide through several international field campaigns (Mammarella et al., 2010; Peltola et al., 2012; Peltola et al., 2014; Rannik et al., 2014), advances in eddy covariance (EC) data processing (Mammarella et al., 2009; Nordbo et al., 2012; Nordbo et al., 2013; Nordbo et al., 2014) and flux gap-filling methods for methane (Dengel et al., 2013).
The EddyUH software, developed in our group, is the state of art tool for EC flux data processing, and at moment counts more than 300 external users. In a recent study (Mammarella et al., 2016), we have carried out an inter-comparison between EddyUH and EddyPro (the software developed by LI-COR Biosciences), aiming to estimate the flux uncertainty due to the use of different software packages and to evaluate the most critical processing steps, determining the largest deviations in the calculated fluxes. In recent study (Rannik et al., 2016), we have reviewed different methods used to estimate random uncertainties of flux measurements by the eddy covariance technique using measured turbulent and simulated artificial records.

Finally, an international field instrument intercomparison was implemented at Lake Vanajavesi (Finland) in January-May 2016 (Potes et al., 2017) and at Alqueva Reservoir (Portugal) in June-September 2017. The aim is to evaluate the performance of a new eddy covariance (EC) instrument called IRGASON (Campbell Scientific), with a separated and standard EC system for reference (Metek + LI-7200). The IRGASON integrates an open-path gas analyzer and a sonic anemometer into the same sensing volume, thus eliminating sensor separation in comparison to the traditional open-path EC setup. However, the first studies made using the IRGASON yielded some unrealistic results (e.g. night-time CO₂ uptake over lakes and vegetation), which seems to be related to a “missing” gas analyser spectroscopic correction (Bogoev et al., 2014).

ECOSYSTEM PROCESSES AND FLUX STUDIES

Boreal forest and carbonyl sulphide flux

Carbonyl sulphide (OCS or COS) is the most abundant sulphur-containing trace gas in the atmosphere. It is mainly produced by oceans and atmospheric oxidation of carbon disulphide (CS₂) and dimethyl sulphide (DMS) and is taken up by oceans, soils and vegetation. OCS has been suggested as a proxy for photosynthesis, as it is an inert compound depositing via stomata and there is no respiratory-like flux back from plants. Continuous OCS flux measurements by the eddy-covariance technique above the canopy (at 23 m above ground) started in April 2013 in the boreal forest research site SMEAR II in Hyytiälä, Finland. A Quantum Cascade Laser (QCL) mini monitor (Aerodyne Research Inc., Billerica MA, USA) has been deployed, measuring OCS, as well as carbon dioxide (CO₂), water vapour (H₂O) and carbon monoxide (CO). OCS fluxes in Hyytiälä show similarities with few other flux studies. Especially, the forest is a significant sink during the growing season day-time and the observed OCS fluxes correlate well with the gross primary productivity estimated from the observed CO₂ fluxes (Erkkilä et al., 2016). We performed two campaigns in the summer of 2015 and 2016 at the SMEAR II site to provide better constrained OCS flux data for boreal forests, related in particular to the role of soil and to the seasonal variation of Leaf Relative Uptake (LRU) ratio needed for estimating photosynthesis (GPP) from OCS fluxes. A combination of OCS measurements was made during both years, i.e. atmospheric profile concentrations up to 125 m, eddy-covariance fluxes and soil chamber fluxes. In addition to these, branch chamber measurements were done in 2016 in an attempt to observe the LRU throughout the whole season. We found that LRU is highly light-dependent and night-time ecosystem uptake of OCS is due to soil microbial uptake and incomplete stomatal closure in the leaves. The full budget of OCS will be considered by scaling up the soil and branch measurements to the ecosystem level.

In spring 2017 we had a joint field campaign with Optics of Photosynthesis Laboratory and University of Groningen in SMEAR II research site in Hyytiälä. By comparing photosynthesis dynamics measured with both fluorescence and OCS exchange at ecosystem and leaf levels, we hope to get new insights into the less understood photosynthetic and respiration dynamics.

Greenhouse gas exchange over lake

Freshwaters bring a notable contribution to the global carbon budget by emitting both carbon dioxide (CO₂) and methane (CH₄) to the atmosphere. Since 2010 our research activities is carried out at the comprehensive and unique measurement platform Lake-SMEAR, located in the small boreal Lake
Kuivajärvi, close to Hyytiälä Forestry Field Station in Southern Finland. Lake-SMEAR includes direct and indirect flux measurements of CO₂ and CH₄ and other auxiliary measurements over the lake and in the water (Mammarella et al., 2015). We aim to assess the current global CO₂ evasion estimates from lakes to the atmosphere by comparing parameterizations for gas transfer velocity k and the significance of wind and heat flux to the gas transfer especially in small lakes (Heiskanen et al, 2014). Global estimates of freshwater emissions traditionally use a wind speed based gas transfer velocity k (e.g. Cole and Caraco, 1998), for calculating diffusive flux with the boundary layer method (BLM). Such simple parameterizations are also often used in lake models including carbon cycle related processes (e.g. Stepanenko et al., 2016). For slightly soluble gases, like CO₂ and CH₄, k is mainly controlled by waterside turbulence. We investigate the relationship between water-side turbulence and the air-water gas transfer velocity k using in-situ measurements performed at Lake Kuivajärvi in Southern Finland. Direct measurements of water-side turbulent velocity fluctuations were obtained with an Acoustic Doppler Velocimeter (ADV), from which water surface dissipation of turbulent kinetic energy (ε) was calculated. Simultaneous observations of k were obtained using measurements of CO₂ and CH₄ fluxes performed with eddy covariance and floating chamber methods, together with dissolved gas concentrations (pCO₂ and pCH₄) measured at the water surface. Field measurements of k are compared to the small-eddy model and other theoretical approaches, which relate the efficiency of a gas to escape from the water-air interface (e.g. the gas transfer velocity) to near-surface water turbulence expressed, for an homogenous surface layer, by ε (Mammarella et al., 2017). Other recent studies include two important aspects: 1) the effect of water clarity on thermal stratification of a lake, which in turn affects lake-atmosphere heat exchange and further gas transfer (Heiskanen et al., 2015); 2) comparison of fluxes of CH₄ and CO₂ measured during a two week campaign at Lake-SMEAR using different techniques, including eddy covariance, floating chambers, and direct measurements of water turbulence and k (Erkkilä et al., 2017). The agreement between different methods were fairly good, and recent parameterizations for k, including both wind and heat fluxes (Heiskanen et al., 2014; Tedford et al., 2014), were superior in comparison with more simple ones (e.g. Cole and Caraco, 1998).

**New flux tower in West Siberia peatland**

In order to fill one of the major observational gaps, we have established recently a new eddy covariance flux tower at the raised bog wetland site at the Mukhrino field station in Khanty–Mansi Autonomous Okrug (Russia). The flux tower for energy, carbon dioxide fluxes is the first one in West Siberian peatlands (with the nearest one being ZOTTO 1000 km to the east). The fluxes obtained in summer-2015, combined with the available meteorological, soil and vegetation data are used to study the diurnal and seasonal variations of fluxes, as well as to determine ecosystem annual budgets of energy and carbon at this typical Siberian middle taiga bog site (Alekseychik et al., 2017). The measurements continued in 2016. In 2018, an extension of the EC system with a CH₄ open-path analyser is planned.

**MODELLING STUDIES**

**Modelling of the urban atmosphere**

Urban areas cause a true challenge for atmospheric modelling due to the highly variable surface by means of both roughness elements, such as buildings and trees, and emission sources. Also, often meteorological forcing data are not available in temporal and spatial scale needed for realistic modelling of the urban atmosphere. A recent study examined the effect of using re-analysis forcing data in local scale hydrological modelling in urban areas using the SUEWS (Surface Urban Energy and Water balance, Järvi et al. 2011) model and what kind of data corrections are needed. Precipitation of these gridded products was found to be the most vital variable to be downscaled to the area of interest using bias correction for quantile mapping (Kokkonen et al. 2017). The same model was also used to examine how warmer winters will modify the wintertime hydrological cycle in cities located in cold climate regions (Järvi et al. 2017).
We are also using a large eddy simulation (LES) model PALM (Maronga et al. 2015) to examine the high spatial and temporal variability of air quality within urban landscapes (Kurppa et al. 2017). Current developments include an integration of aerosol dynamics model to PALM so it could be used in more detailed air quality modelling.

Wetland methane model

We have developed a model of peatland methane (CH₄) emissions, HIMMELI (HelsInki Model of MEthane buiLd-up and emLission). It is not a full peatland model but a module that can be combined with a biosphere/soil carbon model since it needs as input the carbon input rate, i.e., rate of anoxic peat respiration. In addition, HIMMELI needs as input the peat temperature profile, leaf area index (LAI) of aerenchymatous gas-transporting vegetation and water table depth (WTD). HIMMELI simulates microbial and transport processes that take place in the peat column, divided into layers, keeping track on the concentration profiles of CH₄, O₂ and CO₂. The output is fluxes of CH₄, O₂ and CO₂ between the soil and the atmosphere, with the possibility to separate the contributions of the three different transport routes (diffusion, ebullition and plant transport) as well as the fraction of oxidized CH₄. The novelty of HIMMELI is that it has been developed independent of a full peatland carbon model, with the ambition to obtain a robust and flexible model that can be easily used as a tool within different environments. We have run sensitivity tests on the model, as well as tested it on the peatland flux measurement site Siikaneva (Raivonen et al. 2017, Rinne et al. 2007). HIMMELI has also been calibrated for the Siikaneva site using the MCMC methods (Susiluoto et al. 2017) and it has been used as a platform for comparing different ebullition algorithms (Peltola et al. 2017).

Modelling of water vapour exchange by plants

We used theoretical calculations and modelling to show how the reduction in the vapour pressures affects transpiration and carbon assimilation rates (Vesala et al. 2017). Our results indicate that the reduction in vapour pressures of water and CO₂ could enhance plant water use efficiency up to about 10 % at a leaf water potential of -2 MPa, and much more when water potential decreases further. The low water potential allows for a direct stomatal water vapour uptake from the ambient air even at sub-100 % relative humidity values. This alone could explain the observed rates of foliar water uptake by e.g. the coastal redwood in the fog belt region of coastal California provided the stomata are sufficiently open. The omission of the reduction in the water vapour pressure causes a bias in the estimates of the stomatal conductance and leaf internal CO₂ concentration based on leaf gas exchange measurements. We recommend that manufactures of leaf gas exchange measurement systems should incorporate leaf water potentials in measurement set-ups. For other results on studies of tree hydraulics, see the abstract by J. Bäck and T. Hölttä.

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INTRODUCTION

Atmospheric aerosols affect both the climate and human health. Hence they are in a key role when the wellbeing of humans and the environment is considered. The research of the UEF Aerosol Physics Group is focused on atmospheric aerosol particles, both from natural and anthropogenic sources, and especially on their effect on atmospheric processes and further on climate. We are using experimental and modelling methods to study the formation and evolution of particles in the atmosphere and the role they play in the Earth’s climate through their interactions with clouds.

GROUP ACTIVITIES

The group’s experimental research is focused on studies on physical and chemical characteristics of aerosol particles, and especially on their interaction with water vapour. Recently we have been performing measurements both in atmospheric measurement campaigns in different environments and in the laboratory utilizing environmental chambers designed for aerosol formation studies. The focus of these campaigns was in:

- Transformation of organic aerosols in clouds (Väisänen et al., 2017; Reed-Harrison et al., 2017; Wagner et al., 2017)
- Water up-take and CCN and IN activation of atmospheric aerosols (Zieger et al., 2017; Rastak et al., 2017; Korhonen et al., 2017)
- Interactions between anthropogenic and biogenic emissions (Kari et al., 2017a and 2017b)
- Formation and characteristics of SOA particles (Yli-Juuti et al., 2017; Pullinen et al., 2017; Li et al., 2017; Buchholz et al., 2017; Faiola et al., 2017; Schobesberger et al., 2017)

To investigate these topics more detailed we performed intensive measurement campaigns using our own facilities: The ILMARI facility in studying the interactions between anthropogenic and biogenic emissions, and the Puijo SMEAR IV cloud station to study aerosol-cloud interactions. We ran extensive laboratory measurement campaigns in our Aerosol Physics Lab to study factors controlling the evaporation of SOA particles. Related to this topic, we combined the process modelling and experimental work in the most beneficial way. Very recently we finished two major campaigns in our Aerosol Physics lab: one investigating the evaporation of SOA particles at lowered temperature (Li et al., 2017) and one designed to study how representative model a-pinene SOA is for organic particles in boreal forest environment. Currently we are preparing our ILMARI facility for TNA activity related to the EUROCHAMP2020 project. In addition, related to EUROCHAMP2020 we have performed intensive chamber characterization for our chamber facilities. The group is also participating in the CLOUD12 campaign in CERN taking place this autumn.

The modelling activities of the group have been focused on process modelling levels and the main topics are currently:

- Thermodynamics and transport of organic compounds in gas and particle phase (Yli-Juuti et al. 2017a; Tikkanen et al. 2017a, Mohr et al., 2017; Yli-Juuti et al., 2017b)

Keywords: aerosols, clouds, experiments, modelling
• Development of numerical methods to estimate SOA properties as well as aerosol dynamics details from laboratory and/or atmospheric experiments (Yli-Juuti et al. 2017a; Tikkanen et al. 2017a)
• Development of aerosol description in climate models (Kuhn et al., 2014)

Our main idea is to connect the process modelling and experimental work so that the best possible support both for experimental activities as well as modelling activities is achieved.

COLLABORATION

The group’s excellent research facilities and wide collaborative network allow us to integrate the laboratory and outdoor measurements with theories and models in order to understand and predict the impacts of human-caused and natural changes on climate. Our main collaborators related to the current and near future activities are listed below:

• FCoE teams
• Prof. Ilona Riipinen, & Assist. Prof. Claudia Mohr, University of Stockholm, Sweden
• Prof. Paul Davidovits, Boston College; USA
• Prof. Douglas Worsnop, Aerodyne Research, USA
• Prof. Joel Thornton, University of Washington
• Prof. Sergey Nizkorodov, University of California, Irvine, USA
• Prof. Gordon McFiggans, University of Manchester; Great Britain
• Prof. Alex Gunther, University of California, Irvine, USA
• Prof. Frank Stratmann, Leibniz Institute of Tropospheric Research, Germany
• Prof. Jarmo Holopainen, UEF, Finland
• CLOUD collaboration

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REFERENCES


THE DEVELOPMENT OF CHAMBERS AT SMEAR II: THE PURSUIT OF COMBINING NOVEL SCIENTIFIC METHODOLOGY, RELIABILITY AND EASE OF USE

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KEYWORDS: CHAMBER, ENCLOSURE, PHOTOSYNTHESIS, GAS EXCHANGE

INTRODUCTION

Various types of measurement chambers, enclosing a confined part of ecosystem under observation, have been utilized at Hyytiälä forestry field station for almost 50 years. This abstract introduces the central dynamic chambers used at SMEAR stations within the last 10-20 years, and discusses their advantages and disadvantages, especially from practical point of view. Also non-dynamic chambers are discussed, because it shares the similar technical platform with the dynamic chambers. The main attention is paid to the technical and practical development of chamber construction.

Chamber method is used for studying the gas exchange of the part of ecosystem under observation. The estimate on gas exchange can be utilized for upscaling the detected fluxes over larger areas, or for studying the responses of exchange rates on environmental factors such as temperature and solar radiation. The measurement method of gas phase substances depend largely on sample gas properties, affecting sampling method and gas analyser for example, but naturally also study object and interface have an effect too. In the case of chamber measurements, a piece of ecosystem (‘study object’) is enclosed inside a chamber (‘interface’), from which gas samples are collected via tubes and valves (‘sampling method’), and finally gas concentrations are analyzed using for example an infrared gas analyser or a mass spectrometer (‘gas analyser’). Chambers are designed in such a way that the flux of target gas can be determined based on the change in concentration during a chamber closure.

The chambers used at SMEAR stations can be divided into three groups, based on the study object. Soil chamber is placed on the top of soil, usually with a suitable collar, enclosing inside a patch of soil and typically also some surface vegetation. Stem chamber is installed on or around a tree stem, enclosing inside a patch of bark as well as lichens, mosses and other organisms living on or inside the bark. Shoot chamber is installed in such way that leaves or needles or part of them, as well as typically a piece of branch is enclosed inside the chamber.

In the context of SMEAR stations, most chambers are transparent for visible light, but especially among soil chambers dark ones are used as well. Also the transparent chambers may be obscured every now and then to study the responses under darkness and/or to widen the temperature range in measurements. To ensure contact with ambient conditions, the chambers often include some opening parts such as lids or hinged boxes; those are typically operated pneumatically, but also electric linear and gear motors have been utilized. The gas concentration analysis takes most often place outside the chamber, with a specialized gas analyzer, for which sample air has to be pumped from chamber. Over the years, at least CO\textsubscript{2}, H\textsubscript{2}O, NO, NO\textsubscript{x}, O\textsubscript{3}, wide array of volatile hydrocarbons, CO, and $^{13}$C in CO\textsubscript{2} have been
continuously measured or tested. Chamber measurement methodology used at SMEAR stations has been widely explained for example by Pumpanen et al. (2001 and 2015), Altimir et al. (2002), Raivonen et al. (2003) and Kolari et al. (2012).

Figure 1. An example of CO\textsubscript{2} and water vapour concentrations during a one minute closure of a chamber housing a Scots pine shoot during a summer day. Photosynthesis exceeds respiration, and CO\textsubscript{2} concentration inside the chamber tends to decrease, while transpiration yields increase of water vapor concentration in the chamber airspace.

CHAMBERS

Soil chambers

1. Cylindrical soil chamber
   - Soil and forest floor vegetation CO\textsubscript{2} and water vapor flux measurements from 1995 until summer 2009.
   - Poly(methyl methacrylate) (PMMA), wall thickness 5 mm.
   - Volume 5.6 dm\textsuperscript{3}, soil surface area enclosed 0.028 m\textsuperscript{2}.
   - Pneumatically operated lid.
   - No collar, the lower end of the cylinder is pushed inside the humus layer.
   - Inner surfaces often covered with fluorinated ethylene propylene (FEP) film to decrease the effect losing substances to chamber walls of wall losses.
   - Construction and made by Metallityöpaja Toivo Pohja.
   - Imperfect tightness against soil, leading to tendency to occasional underestimation of the true soil respiration.
   - Low representativeness due to the small soil surface area enclosed inside the chamber.

2. Large VOC soil chamber
   - Primarily for soil and forest floor vegetation VOC flux measurements starting from 2010, secondarily for CO\textsubscript{2} and water vapour fluxes.
   - Pneumatically operated.
   - Aluminum frame, FEP foil walls.
   - Steel collar, ensuring sufficient tightness against soil.
3. ToHeLi soil respiration chamber

- Soil and forest floor vegetation respiration since 2009.
- Static chamber, CO₂ concentration measured with Vaisala GMP343 probe inside the chamber.
- PMMA walls, aluminum collar.
- Operated with pneumatics or electric gear motor.
- Typically obscured using aluminum foil, to prevent photosynthesis during closures.
- Volume 12.5 dm³, soil surface area enclosed 0.05 m².
- Construction by Toivo Pohja, Heikki Laakso and Liisa Kulmala, made by Toivo Pohja and Heikki Laakso.
- High quality respiration data; due to small area enclosed represents only very limited soil patch. This increases the representativeness.

Stem chambers

4. Original stem box chamber

- Stem CO₂ efflux measurements since 1990s until 2012.
- Made of PMMA, sealing with chloroprene seal against the tree stem.
- Volume 0.04 dm³, stem surface area enclosed 0.0002 m².
- Operated at steady state.
- Construction and made by Toivo Pohja.
- Low chances to utilize in any other use than in CO₂ efflux measurement.
- The thick chamber walls and lack of contact with ambient air lead to tendency to affect the environmental properties such as temperature and humidity.

5. Spiral type stem chamber

- CO₂ efflux and VOC emission measurement since 2012 until 2016.
- A piece of Eaton Synflex 1300 polyethylene-aluminum composite tube winded around the tree stem; FEP foil cover and an aluminum plate for inlet and outlet fittings.
- Construction by Toivo Pohja, Anni Vanhatalo and Pasi Kolari, reusable parts made by Toivo Pohja.
- The enclosed stem surface area and volume vary between the chambers, but the ratio between the stem surface area and volume is rather high, allowing sufficient signal for VOC emission measurements.
- The spiral-type structure was chosen to ensure sufficient air mixing, but mixing is still rather weak and problems caused by high humidity inside the chamber are common.

6. Stem chamber with opening lids

- CO₂ efflux and VOC emission measurements since 2016.
- Two pieces of bent aluminum frames with pneumatically operated lids and fans, and n pieces of smaller aluminum frames supporting the FEP foil apart from the tree stem.
- The enclosed stem surface area and volume vary between the chambers.
- Construction by Toivo Pohja and Juho Aalto, reusable parts made by Toivo Pohja.
- Conditions inside the chamber stay close to ambient between the closures; also humidity problems are to large extent avoided.
- Because of the sufficient mixing and minor alteration of conditions inside the chamber, data quality of both CO₂ and VOC measurements is higher than with the previous chamber types.

**Shoot chambers**

7. Cylindrical chambers
- In use since 1986.
- CO₂, water vapour and other gas flux measurements, including VOCs.
- PMMA tube of 14.4 cm inner diameter, volume 3.5 dm³; inner surfaces typically covered with FEP film.
- Two pneumatically operated lids, small one with a fan and large one to ensure sufficient contact with ambient air between the closures.
- Construction by Juhan Ross, Perti Hari and Metallityöpaja Toivo Pohja, made by Metallityöpaja Toivo Pohja.
- Rather well suitable for VOC measurements also because the shoot or leaves are not disturbed by squeezing to plane.
- Rather high volume, limiting the measurement of low gas exchange signals.
- Shoot is not facing fully ambient conditions such as rain or UV radiation.
- Cylindrical structure is versatile, allowing variants such as shorter or longer chamber or inclusion of detailed light environment measurement either inside or outside of the chamber.

8. Box chamber
- CO₂, water vapour and other gas flux measurements
- In use starting from 1997 until the early 2000s.
- Supporting frame for installing the chamber to tree stem so that the tip of a shoot is inside the chamber.
- Quartz top plate and PMMA walls.
- Volume 1 dm³.
- Two pneumatically operated lids with fans under the chamber.
- Shoot squeezed to plane between special net structures to simplify the light environment and to reduce the chamber volume.
- Construction and made by Metallityöpaja Toivo Pohja.
  Temperature stays rather high between the closures because the interior of the chamber is flushed with ambient air through the bottom plate holes only.

9. Old slide chamber
- In use since 2004.
- CO₂ and water vapor flux measurement, in case of deciduous trees also VOC measurement.
- Supporting frame for installing the chamber to tree stem so that the tip of a shoot is inside the chamber.
- 5 mm and 3 mm thick PMMA walls; top plate UV-transparent (3 mm Röhm Sunactive 2458 PMMA); inner surfaces typically covered with FEP film.
- Housing for radiation sensor inside the chamber.
- Shoot squeezed to plane between special net structures.
- The chamber opens pneumatically by sliding the box open and exposing the shoot to ambient conditions.
- Construction and made by Toivo Pohja.
- Ventilation is efficient, volume is optimized.
- High quality gas exchange data but not suitable for VOC measurement in case of Scots pine.

10. New slide chamber
- Measurement of shoot or leaf gas exchange since spring 2017.
- The structure is otherwise the same as in case the old slide chamber, but the volume is increased to 2.1 dm³ to allow installing of free shoot, and the walls are put together with
screws instead of gluing, allowing easier coating with FEP film.
- Shoot either squeezed to plane or installed without squeezing.
- Construction by Metallityöpaja Toivo Pohja and Juho Aalto, made by Tauri Tätte, University of Tartu.
- Suitable for a wide variety of applications, including VOC measurement of all tree species.

CONCLUSIONS

Comprehensive and long-term field observation of gas exchange requires the use of a wide variety of different kinds of chambers. When the aim is to conduct automated, continuous measurements, the standard should be the best technical solutions and high quality assembly and finishing. Once chambers are made of appropriate materials and they are maintained regularly and duly, they endure in good working condition for years. One good example of durability are the shoot chambers at SMEAR I in Värriö: after hundreds of thousands of chamber closures, the chambers dating from 1990s work daily fine. Thus, even subarctic conditions, where yearly temperature range exceeds 50 °C and weather changes are continuous, are not an obstacle to conduct continuous chamber measurement through the seasons.

It’s obvious that developing and building new measurement chambers requires a team of skilled technicians, conversant researchers and seamless collaboration between those. That has often succeeded at SMEAR stations. As the best solutions do not necessarily turn up at once, the chamber development is a continuous, self-reconstructing process, which produces better and better solutions in the course of years.

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QUALITY CONTROL BY PERFORMANCE AUDITS IMPROVING THE QUALITY OF ATMOSPHERIC GREENHOUSE GAS MEASUREMENTS

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Keywords: GREENHOUSE GASES, QUALITY CONTROL, ICOS

INTRODUCTION

Climate change and its mitigation measures are created a demand for accurate, long term and spatially extensive greenhouse gas measurements. European wide ICOS (Integrated Carbon Observation System) research infrastructure is answering this demand by creating an extensive network of measurement stations. ICOS concept is a high precision long-term network of stations measuring greenhouse gas concentrations in the atmosphere and greenhouse gas fluxes from ecosystems and oceans, designed around central facilities (CF). The main tasks of CFs are provision of calibration gases, standardized data processing, technical support and training, and quality control (QC). For fulfilling of the data quality objectives, QC is essential part of the measurement procedures in ICOS. The ICOS atmospheric station network QC is split into three different hierarchies: station internal QC, ICOS internal QC and ICOS external QC. Mobile laboratory (MobileLab), established under Atmospheric Thematic Centre (ATC) and operated by Finnish Meteorological Institute (FMI), represents ICOS internal QC. The main purpose of the MobileLab is to ensure the high quality measurements and data of atmospheric stations by helping the station personnel to achieve and maintain the high level of station’s operation. In practise, the MobileLab performs audit visits to the stations in order to evaluate the data quality and to find out the possible ways to improve the station’s performance.

MOBILELAB CONCEPT

The MobileLab is permanently equipped with two travelling instruments; 1) Picarro G2401 cavity ring-down spectrometer (TI-G2401 hereafter) to measure CO₂, CH₄, CO and H₂O concentrations (Rella et al., 2013) and 2) Ecotech Spectronus FTIR (Fourier Transform InfraRed spectrometer, TI-FTIR hereafter) for CO₂, CH₄, CO, N₂O and H₂O measurements. FTIR is not qualified by the ICOS at the moment, but since its measurement technique deviates from the Picarro G2401, it serves as a good reference, and when FTIR also measures a wide range of components, its usage is reasonable for the audit purposes (Griffith et al., 2012; Hammer et al., 2013a; Hammer et al., 2013b).

For the audit measurements, the MobileLab uses travelling standard cylinders (TSs) prepared by FMI and calibrated against laboratory standards (WMO CCL scale) prepared by WMO Central Calibration Laboratory in NOAA (National Oceanic and Atmospheric Administration, USA). The fact that the preparation of the MobileLab TSs is separated from the ICOS Central Analytical Laboratory (CAL), which provides standard gases for the stations, gives an external and independent nature for the MobileLab audits. The stability of the FMI laboratory standards, however, is ensured with regular cross-checks against the ICOS primary standards maintained by CAL (Fig. 1).
Figure 1. Fit residuals of the five laboratory standard cylinders over three year period indicate good stability of the cylinders. Laboratory standards are prepared by WMO Central Calibration Laboratory in NOAA, USA and calibrated in WMO CCL scale.

For the intercomparison measurement during the audits, the MobileLab instruments will sample from the highest level through the mandatory spare inlet. As MobileLab activities should not to disturb local permanent measurements, it does not use the same sampling line with local instrument. If station has recognised problems with other sampling heights, inlets or manifolds, part of the audit visit can be spent to resolve these issues. The intercomparison measurement including to the audit continue approximately two months, depending on the local circumstances. In addition to the intercomparison measurement with the local instrument, also the other equipment of the station will be checked; such as meteorological sensors, sample inlets and manifolds; that they meet the ICOS requirements. After the audit visit at the station, the MobileLab prepare a report in conjunction with the station PI, which includes also possible suggestions to improve the station operation and data quality.

The MobileLab has a quality system including standard operating procedures (SOPs) for all its operations. That ensures the reproducible audit visits from station to station still enabling the MobileLab to adapt its operation to the local specialities. The MobileLab SOP includes also the off-station operation, i.e. the preparation of instruments and calibration gases before the audit visits as well as the maintenance of instruments and equipment.

MOBILELAB AUDITS

The MobileLab have been planned to perform 2–4 ICOS atmospheric stations audits per year. During the first four years the MobileLab has been operational, it have made seven audits, mainly due the lack of operational stations during this preparation phase of ICOS. So far the MobileLab has audited following stations: Smear (SMR, Finland) two times, OPE-Andra (OPE, France), Jungfraujoch (JFJ, Switzerland),
Hohenpeissenberg (HPB, Germany), Puy de Dome (PUY, France) and Křešín u Pacova (KRE, Czech). Only four of the stations (HPB, PUY, KRE and SMR) have had official ICOS standard gases during the audit. Also the instrument status has not been final in some stations. However, even though the MobileLab has not been audited the final set-up of certain stations, the visits have been valuable practise for the MobileLab procedures and personnel.

Calibration Cylinder Cross-Measurement

The strategy of ICOS to maintain the same calibration level for all the atmospheric stations is possible by using the calibration gas cylinders prepared by the CAL solely. In this case preparation includes both filling the cylinders as well as determining their gas concentrations. One of the key operations during the MobileLab audit is the cross-measurement of the MobileLab TSS and local standard cylinders. As the correctness of the ambient greenhouse data is largely depending on calibration gases and procedures, it is essential to check that gas concentrations of local calibration cylinders still represent the concentrations assigned by CAL. During the cross-measurement, also the expertise of local personnel to measure gas cylinder can be evaluated.

Since the CAL was not operational at the time the MobileLab made first audits, the origin of the calibration cylinders of the stations varied. However, the cross-measurement of the cylinders was still performed during the audits. In calibration cylinder cross-measurements of CO₂ and CH₄ it was not able to see whether calibration cylinders were filled and calibrated by CAL or not, but with CO the CAL fingerprint was clear. The cross-comparison results of CO with cylinders provided by CAL remained always below the GAW compatibility goal (±2 ppb), which was not the case with cylinders from various origins.

Intercomparison measurement of ambient air

Together with calibration cylinder cross-measurement, ambient air intercomparison measurement is a key procedure of the MobileLab audit. To ensure dataset large enough for comparisons and statistics, intercomparison measurements last from one and a half to two months. The long measurement period also enables different kind of weather events (i.e. variation in air pressure, wind, and temperature, precipitation events…) during the audit to check that there is no systematic errors related to measurement conditions. As already mentioned, the MobileLab uses spare inlet line for intercomparison measurement, also if mixing volumes or sample dryer(s) are applied for local measurements, sample air for the MobileLab instruments is not directed through to those parts. The TI-FTIR has its own drying system (Nafion® followed by magnesium perchlorate), so it measures always dried air, whereas the TI-G2401 measures as wet and the data is water vapour corrected by factors determined during each audit.

All the raw data from ICOS atmospheric stations is uploaded to ATC server and calculated there (Hazan et al., 2016), whereas MobileLab calculates the data from its own instruments independently. Since the final data released from ICOS Carbon Portal for end-users is hourly averaged, the MobileLab is also using hourly averages when comparing results of intercomparison measurements. Another reason to use hourly averaged data for comparisons is to minimise the effect of differing sample residence times caused by differences in sample lines and instrumentation between the atmospheric stations and the MobileLab.

Even though the MobileLab ambient air measurements differ from station permanent measurements in regards of sampling line and possible sample pre-treatment, the magnitude of the deviation found between local calibration cylinders and TSS in most cases correspond the deviation in ambient air intercomparison measurements. The largest deviations in standard cylinder and ambient air measurements between the MobileLab and atmospheric stations are commonly found in CO measurements that is the trickiest one of these three mandatory component to measure.
CONCLUSIONS

From 2014 onwards, the MobileLab has set up its instrumentation, developed its operating procedures, quality system and reporting, and conducted seven audits. So far, the ICOS atmospheric station network has been under the building stage, but during 2017 the first stations will accomplish the labelling process. Due to the building stage of the atmospheric stations as well of the MobileLab, the frequency of audit visits has remained below the initial plans during these first years of operation. However, the audits performed at the stations with varying level of readiness have proven the high overall level of measurement performance, but also revealed some drawbacks in the chain from measurements to data processing.

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TOWARDS AEROSOL CLIMATOLOGY USING NIGHTTIME AOD MEASUREMENTS

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Keywords: Lunar measurement, AOD, aerosol.

INTRODUCTION

To obtain characteristic information on aerosols and their effect on climate, it is essential to have a global network with long-term measurements for aerosol climatology. Global AERONET (Aerosol robotic network) is one example of international collaboration resulting in fruitful studies of aerosol properties. Conventional ground based photometry for aerosol optical depth (AOD) retrieval is based on utilization of sun radiation as a light source. Applicable data requires continuous sunlight at a direction of measurement, cloud-free sky, and a sun elevation high enough. However, a reliable deduction is lacking the data from dark period including both nighttime and polar night. Recent achievements on the measurement techniques with enhanced signal amplification and better signal to noise ration have led to a possibility to extend to the measurement cycle with nighttime measurements using Moon light as a light source. Finnish Meteorological Institute (FMI) has recently deployed two new Lunar type photometers CIMEL CE-318T for continuous AOD and water vapor measurement. In addition to conventional daytime direct sun measurements, it is able to perform nighttime measurements to obtain nocturnal variation of AOD and to extend the seasonality of the data with wintertime measurements. In this study, we present an example of very first instrument tests in Helsinki and Sodankylä.

METHODS

Standard CIMEL CE-318 sun photometer (Holben et al., 1998), so far the most wide-spread and scientifically validated multiband photometer for ground based AOD and the general instrument within AERONET, lacks the ability to measure at low sun angles due to low amount of solar intensity and high diffuse light. As the passive photometry needs a bright light target to point, solutions for nighttime AOD measurements have relied on very expensive and labour consuming star photometers.

Physically the new triple type instrument, CIMEL CE318-T Sun Sky Lunar photometer looks almost the same as the standard Cimel version. Noteworthy differences between the new and old photometers are enhanced signal amplification and a lunar tracker on the Lunar photometer. The stability of the Lunar photometer is similar to the standard Cimel photometer. Since highly changeable moon’s illumination is inherent to the lunar cycle, traditional Langley calibration is not possible. Instead, a modified method, caller Lunar-Langley, is used. This requires the extraterrestrial irradiances from a lunar irradiance model. Final results provide similar accuracies on AOD as those of AERONET (± 0.01– 0.02). At the moment, CIMEL CE318-T is the only lunar photometer which is supported by AERONET (Barreto et al., 2013)

In this study we give an example of AOD measurements performed during the test phase of Lunar photometer #535 in Helsinki and Sodankylä, with both places having an independent standard photometer for comparison. From the standard Cimel data, we have picked the daylight data achieved near sunrise and sunset. AOD was measured at 9 channels between 340 and 1020 nm. Figure 1 shows the AOD measured with Lunar photometer #535 in Sodankylä between 6th and 7th September, 2017. The data between 19:25-22:05 UTC was achieved using Moon as light target. No data during dusk and dawn were available due to absence of light target during that time.
CONCLUSIONS

Taking into account the instrument accuracy of $\pm 0.01$–0.02 and the fact that sun and moon AOD are measured with a different instrument amplification, the night AOD fits rather well with the evening and morning AOD. The sawtooth pattern shown in green colour is from the 380 nm channel, which has a very poor signal for Lunar measurements. Normally the shortest wavelength for moon-AOD should be 440 nm. To conclude, Lunar photometer is a good addition for measurement setup to complete the aerosol datasets.

Figure 1. AOD between 2017-09-06 and 2017-09-07 in Sodankylä. The time is in UTC.

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LONG-TERM FIELD MEASUREMENT WITH PARTICLE SIZE MAGNIFIER (PSM)

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Keywords: PSM, CPC, long-term operation

INTRODUCTION

Reliable and reproducible measurements are one of the key interests in the quest of gathering knowledge about atmospheric new particle formation. There are several undertakings to provide working practices and code of conducts for creating measurement infrastructures and performing measurements in as comparable as possible way. These are research entities, like Integrated Carbon Observation System (ICOS) and Aerosol, Cloud, and Trace gases Research InfraStructure Network (ACTRIS), which give guidelines to carry out, for example fundamental measurements like number concentration of cloud condensation nuclei (CCN) using a CCN counter or particle size distribution measurements using a Differential Mobility Particle Sizer (DMPS).

Instrumentation to measure newly formed particles, neutral and charged, down to a size close to 1 nm has been now available for some years. Airmodus A11 nCNC has been used in numerous sites all around world (Kontkanen et al., 2017) and in the future it will most likely be one of the standard equipment in forthcoming field campaigns and research stations. Still, there is not yet well documented practice to do these measurements with the A11. In this work we are trying to provide some insight on what kind things should be dealt with while doing long term measurements with PSM or other condensation based device using diethylene glycol (DEG) as a working fluid.

METHODS

Big part of the knowledge that is collected here is based on knowhow that has been gathered during the past few years, while we have implemented the Airmodus A11 nCNC (Vanhanen et al., 2011) as a permanent measurement in the SMEAR II (Hyytiälä) and III (Helsinki) and just recently to SMEAR I at Värriö. There is also a lot of development that has been done in the aerosol laboratory at the division of atmospheric science, for example related to the sampling of smallest aerosol particles (Kangasluoma et al., 2016a) and characterization measurements for the PSM (Kangasluoma et al., 2014).

RESULTS/ DISCUSSION

Sampling is one of the key aspects in sub-3 nm aerosol particle measurements. Small newly formed particles will diffuse rapidly and are lost into the sampling lines if special care is not taken. In its simplicity, we want to get the sample as quickly as possible to the instrument without introducing turbulence or unnecessary bends that introduce addition losses (Wang et al., 2002). In addition, tubing needs to be conductive to avoid electrostatic losses which removes charged particles efficiently. We have settled to a sampling system that is described in detail by Kangasluoma et al. (2016a). Shortly, it contains 40 - 60 cm long 10 mm outer diameter steel tube and core sampling with bypass flow. It can also contain electrostatic filter to investigate only electrically neutral particles. With this kind of inlet system, losses in the inlet line are almost negligible. Avoiding losses while sampling becomes even more important when measuring the total particle concentration, instead of number size distributions, since without knowledge on the size distribution there is only a limited means to correct highly size dependent losses afterwards.
When the PSM is used in scanning mode to measure size resolved particle concentrations, the accuracy of the calibration is very important. We use the term calibration, even though it doesn’t mean connecting the measured quantity to a traceable standard. In this context, PSM calibration means measuring the detection efficiency as a function of size and fixing the size conversion from saturator flow rate to particle diameter. How these are used to calculate size distribution from raw data is explained in the paper Lehtipalo et al. (2014). There are a few ways to perform the calibration, in this study we use a glowing wire generator (Peineke et al., 2006; Kangasluoma et al., 2015) with tungsten wire due to its ease of use and reproducibility. The chemical composition and charging state of the test particles affect the detection efficiency of condensation particle counters, and the effect is even stronger with DEG than, for example with butanol (Kangasluoma et al., 2014; Kangasluoma et al., 2016b). This implies that one should have fairly good knowledge about what kind of particles are measured to conduct an accurate calibration. This can be difficult either due to the lack of knowledge about chemical composition of the particles or due to the difficulty to produce calibration particles of interest. One approach is then to accept some ambiguity in the calibration and focus more in making instruments and measurements comparable with each other. Added to the previous, the sample gas properties also affect the detection efficiency. It has been shown that the humidity of the sample air can affect the performance of DEG-based particle counter/size magnifier (Iida et al., 2009; Kangasluoma et al., 2014). Lab measurements show that, when the PSM is used with settings that cause homogenous droplet formation inside the instrument, detection efficiency can be correlated to the background counts (Figure 1). This is true at least for finite background window. We are using this to tune A11 settings on the field, in a way that the detection efficiency would be as close to the laboratory calibration as possible. The amount of background counts are then monitored by automated zero-air measurements which are performed by introducing filtered ambient air to instrument (Kangasluoma et al., 2016a). This is not perfect solution since it seems that the medium conditions affect more to the detection than to the background counts. To improve this we are building portable calibration unit which is in principle a small high resolution DMA (halfmini) (de la Mora and Kozlowski, 2013) in open loop configuration so the carrier gas will match to the ambient conditions.

Figure 1. Detection efficiency of the PSM as a function of background counts. Measurement is with THA+ ion with 1.47 nm mobility diameter (Ude and de la Mora, 2005). PSM’s saturator temperature indicated with color.
In addition to the fundamental challenges that are related to the operation principle, there are a lot of challenges that are due to the fact that the instrument is running for a long time. One of these is excess DEG which accumulates to the lines between PSM and CPC due to condensation. Manufacturer offers drip bottle which is a small bottle that is attached to the vertically aligned Swagelok T-peace. This works by collecting majority of this excess DEG.

Despite this, after extended period of use there is still some accumulation of DEG in inside PSM and before the drip bottle. This will lead to extra background in the CPC which visible in zero-air measurement and might cause premature fouling in the CPC’s optics due to DEG condensation on the lens surfaces.

One of the biggest factors for long-term PSM measurement accuracy is the condition of the CPC. There are several types of malfunctions that might happen to it, which will affect to the measured particle concentrations. Firstly the optics will get dirty after long time, so those need to be serviced time to time. During the field campaigns and our continuous measurements the pulse duration is monitored and plotted (discarding concentrations above 5000 cm$^{-3}$). Sharp decrease of average pulse duration is a good indicator of optics getting dirty which means that the CPC needs to be maintained. Other good parameter to monitor is the flow rate, which show, for example critical orifice getting dirty or possible leakage inside the instrument.

It is important to use consistent methods in the atmospheric measurements. For now, there is still a need to further improve the long-term measurements with PSMs and furthermore, come up with consistent way to perform calibrations for different environments.

ACKNOWLEDGEMENTS

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THE FIRST COMPARISON OF SURFACE EXCHANGE RATES BETWEEN SIIKANEVA FEN AND BOG SITES

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Keywords: peatland, boreal, carbon dioxide, methane, eddy covariance.

INTRODUCTION

Natural boreal mires are represented by two fundamental ecological classes, bogs and fens. The differences between the two have been extensively treated in many studies, however, a fair amount of uncertainty remains as of how their ecosystem-atmosphere exchanges and the consequent climate impacts compare.

Siikaneva is one of the most intensively studied peatland complexes in the Boreal region. The studies targeted surface exchange of carbon dioxide, methane, energy on different scales – from plant to microsite and ecosystem; vegetation dynamics including leaf area index and biomass, peat structure and composition, and so forth. These activities were brought out at two distinctive ecological areas of the peatland, fen and bog. Being separated by a mere 1.2 km distance, the two sites present widely different vegetation, soil structure, surface microtopography and hydrology. Having two sites in such close proximity but within different mire types zones is a unique opportunity to study ecological differences with the absence of the climatic differences.

METHODS

Measurements took place at the Siikaneva-1 station since 2005 and at Siikaneva-2 in 2011-2016, which has correspondingly produced 13 and 6 years of data. However, this study uses only the overlapping years, 2011-2016. In this period, eddy-covariance (EC) data on CO2, CH4 and energy exchange is available, along with the standard meteorological and auxiliary measurements. Leaf area index was measured by the University of Eastern Finland in 2012-2015, although not every year in each of the two sites.

One of the central aspects of this work is the development of the new method for eddy-covariance gas exchange data gapfilling with targeted at the datasites with large and/or frequent gaps. This was prompted by the reality that the data series in both Siikaneva sites are prone to be incomplete to a varying degree every year, more so in Siikaneva-2 than -1. A method was formulated, where the parameters of the empirical response functions are calculated as spline-smoothed discrete values obtained in a moving time window. Figure 1 details the process.

The new modelling method has first been applied to gross primary productivity (GPP) and total ecosystem respiration ($R_e$) data obtained with eddy-covariance by Alekseychik et al. (2017) in a West Siberian bog. The method proved to yield robust values of the GPP and $R_e$ light and temperature response functions and provide an insight into their seasonal courses. A similar modelling approach has been successfully tested on the EC CH4 flux data.
Figure 1. Schematic explanation of the new modelling approach developed in this study, here with the example of gross primary productivity derived from the 2014 data from the Siikaneva-1 site.

Step 1. Evaluate $P_{\text{max}}$ and $k$ from the fits in individual time windows.

Step 2. Interpolate $P_{\text{max}}$ and $k$ to obtain their time series at the resolution of original data (e.g., 30 min).

Step 3. For each 30 min period, calculate $\text{GPP}_{\text{mod}}$ using Eq. 9.

Figure 2. Preliminary growing May-September cumulative NEE, $R_{e}$ and GPP for the Siikaneva 1,2 sites.
RESULTS

Preliminary results show that the Siikaneva fen and bog had rather different exchange rates in terms of NEE and its components GPP and \( R_e \). Both GPP and \( R_e \) are consistently higher in the fen Siikaneva-1 (Figure 2). However, the resulting net exchange of CO\(_2\) is approximately the same in both site, ranging between -40 and -120 gC m\(^{-2}\) for May-September. It should be noted that, while the mean NEEs are of comparable magnitude, NEE in the individual years may be markedly different (Figure 2).

Interestingly, we observed clear temporal variation in the CH\(_4\) flux temperature response function parameters. The first results (not shown) indicate that the parameters of the response function \([\text{CH}_4\text{flux} = F(T_{\text{peat}})]\) are just as variable as those of GPP or \( R_e \). In particular, the evidence of wide variation on a biweekly time-scale is probably related to the variation in the water table and precipitation.

CONCLUSIONS

The early results of the Siikaneva fen and bog surface exchange comparison presented here hint at significant differences in terms of CO\(_2\) exchange responses to weather and the important role of mire ecosystem type. Deeper analyses need to be brought out to shed more light on the reasons of this contrasting behaviour. With the extensive datasets at our disposal, we might be able to tell how important are the differences in vegetation and microform composition of the two sites. On the other hand, there is potential for further development of the described gapfilling method, especially in application to CH\(_4\) fluxes.

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INTRODUCTION

Solar induced Fluorescence (SIF) is rapidly becoming the signal choice for measuring plant productivity from space. SIF is a remote sensing measurement of chlorophyll a fluorescence, which is visible and near infra-red light emitted by chlorophyll molecules. Because the energy absorbed by chlorophyll goes on to power the photosynthetic reaction chain, changes in the efficiency of the photosynthetic reactions are reflected by changes in the relative yield of chlorophyll fluorescence - it is this physiological link that makes SIF a promising remote sensing signal (Porcar-Castell et al. 2014).

SIF is retrieved from space using some variant of the Fraunhofer Line Depth (FLD) method where the signal is measured in spectrally narrow and dark Fraunhofer (or telluric) atmospheric lines. Such an approach is necessary because although chlorophyll a fluorescence is a spectrally broad signal (~650 – 850 nm), it is almost completely obscured by scattered (reflected) radiation under natural skies. Although SIF is retrieved in narrow spectral regions, the shape of the canopy leaving fluorescence spectrum still affects both measurement and interpretation and cannot be ignored, especially if retrievals combine multiple lines. For example Joiner’s et al. (2013) SIF algorithm, which estimates SIF using GOME satellite data and is probably the most widely used global product to date, utilises an a priori constraint on the shape of the canopy leaving fluorescence spectrum to account for the effect of the non-constancy of the emission over the spectral retrieval wavelengths.

It is relatively straightforward to measure chlorophyll a fluorescence spectra emitted by leaves. All that is required is a broad spectrum light source, a low (wavelength) pass filter, and a visible/near infrared spectrometer. However chlorophyll fluorescence emitted from leaves is not the same as that emitted from canopies, as tree/forest structure almost certainly affects the spectral shape at the larger scale (see W. Liu’s abstract in this issue). Unfortunately the leaf measurement approach is difficult to scale for whole canopies, especially under natural illumination, due to the requirement of near zero extrication energy over a certain wavelength (lower bound of emission). Therefore Zarco-Tejada et al. (2003) used an alternative indirect spectral reflectance based method to retrieve a difference spectra that approximated the true spectral fluorescence shape for a whole plant canopy.

Here we show how we can measure canopy leaving chlorophyll a fluorescence spectra directly. The main requirements are: 1/ Measurements carried out at night, where darkness performs the same role as the low pass filter, and 2/ a strong enough wavelength restricted light source. Our measurements of canopy scale chlorophyll a fluorescence spectra were collected this year as part of the Fluorescence Across Space and Time (FAST2017) campaign.
METHODS

Figure 1. Scot pine tree illuminated by measurement light source. These are three colour photographs of the same experimental subject tree taken prior to the fluorescence measurements. Each illumination colour shown above (blue, green, red) was used to excite chlorophyll fluorescence, and resulted in different shaped chlorophyll emission spectra when measured with an above canopy spectrometer. The spectra of the three light colours pictured above are shown in the lower panel of figure 2. It should be noted that the tree shown here is an example tree for illustration purposes, and not the same as that measured.

Measurements were carried out at Hyytiälä forestry field station on 6 September 2017 after sunset. The measurement set-up consisted of an ASD HandHeld spectrometer (ASD-Panalytical, Boulder, Colorado, USA) and a spotlight multispectral LED light source (Beamz BPP210 PAR64, Scotsdale, Arizona, USA), both instrument and light source were mounted at the top of an above canopy scaffolding tower directly above a single mature Scots pine tree canopy. We cycled through different colours of the LED light source, which are shown in Fig. 1, and recorded emission spectra excited by each separate colour. The red excitation spectrum overlapped with the spectral emission region (figure 2), therefore we used measurements of the spectral distribution of the red excitation source in combination with a measurement of canopy reflectance to empirically correct the spectrum for the reflected contribution. Canopy reflectance was measured during daylight hours under natural illumination from the same above canopy position, using the same spectrometer described above, and reflected radiance from a white Teflon panel used as a reference measurement of irradiance.

RESULTS

Night-time measurements of canopy leaving chlorophyll a fluorescence spectra are shown in figure 2. The spectral distribution of the illumination source clearly affects the measurement, with only the blue-excited spectrum showing a pronounced 'double-peak' shape.

When thinking about satellite SIF, it should be kept in mind that these measurements were performed in darkness at a photochemically relaxed (low stress) state. Solar induced spectra emitted during daylight hours would therefore appear slightly differently to those above, due to changes in the relative state of photosystem's I and II, and also due to the spectral distribution of the excitation source (the sun). Our next goals are to collect more observations (both repeats and new canopies), and also to develop a theoretical method to estimate daytime solar induced fluorescence spectra based on our night measurement protocol.
Figure 2 Canopy leaving chlorophyll fluorescence spectra for Scots Pine (Top). Excitation (i.e. LED) spectra, which were measured in the laboratory using a Teflon reflective panel, are shown in the lower panel.

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RESOLVING THE URBAN MICROMETEOROLOGY WITH LARGE-EDDY SIMULATION

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Keywords: Large-eddy simulation, urban surface model, sensitivity study, wavelet analysis.

INTRODUCTION

Pursuing an improved understanding of the turbulent interactions between the atmospheric boundary layer (ABL) flow and built environments, which are characterized by structural, thermal and material complexity, is an essential goal in urban micrometeorology. In a rapidly urbanizing world, this enterprise has become increasingly important as city planning departments around the globe have started searching for ways to improve the air quality and thermal comfort of the ever-increasing number of urban residents by the means of urban planning. This calls for newly targeted research efforts where the focus is shifted more toward directly scrutinizing the near-surface turbulent processes and the detailed turbulent interactions that occur within the urban canopy. In order to obtain reliable predictions on how local changes in the urban plan influence the local conditions, the relevant turbulence physics that lie at the core of the studied phenomena have to be resolved. Such an approach allows the crucial components that govern, for example, pollutant dispersion, street-canyon ventilation, wind and thermal comfort, and dust and snow propagation, to be exposed at their relevant spatial and temporal scales. Thus, it becomes necessary that the flow behaviour within the Urban Roughness Sublayer (URL), where the flow is directly influenced by the roughness elements (i.e. buildings, trees etc.), is investigated at increasingly finer spatial and temporal resolutions. Studies at this level of detail are difficult to accomplish with in-situ measurements due to the practical difficulty of erecting a multitude of measurement sites within densely built urban areas. However, thanks to the modern supercomputing facilities and the availability of accurate airborne Light Detection And Ranging (LiDAR) datasets, these urban flow investigations can be approached by the means of turbulence-resolving computational fluid mechanics, namely, Large-Eddy Simulation (LES).

Turbulence resolving urban flow investigations, which have been performed with LES up to this date have laid a firm foundation for the future investigations. Letzel et al. (2008) carried out a wind tunnel vs. LES investigation employing a uniform array of cubes to represent the urban structures and demonstrated that the sufficient LES resolution to capture the essential flow behaviour between the obstacles (i.e. within the ‘street-canyons’) requires approximately 32 computational points spanning a cube-like building face or the width of a street-canyon. This translates to approximately 1 m resolution in a heterogeneous, densely built urban arrangement typical of a downtown area in a European city featuring perimeter blocks. Giometto et al. (2016) employed 1 m resolution in an investigation featuring a 512 x 512 m section of the city of Basel, Switzerland, around the site, which hosted a measurement campaign and demonstrated through a comparison that experimentally obtained mean flow characteristics could be well captured by the LES simulations. Very recently Hertwig et al. (2017a, 2017b) performed a meticulous validation study featuring a detailed wind tunnel model of the down-town area of Hamburg. Their work involved detailed comparisons at different spatial locations between wind tunnel and LES data. The comparisons revealed that the uniform spatial resolution of 2.5 m in their LES model was insufficient to capture the turbulent structures within the street-canyons, but yielded strong agreement in flow statistics and turbulent structures just above the urban canopy. The aforementioned wind tunnel and LES models did not consider the influence of vegetation (trees particularly), which are an essential roughness element within urban
environments. Giometto et al. (2017) completed an LES investigation on the influence of trees on urban flow by considering a residential area in Vancouver, which also hosts an eddy-covariance (EC) measurement site from which turbulence statistics can be obtained for comparison. The study revealed, as expected, that the trees play a significant role in the momentum exchange between the atmosphere and urban surface, thus, emphasizing that trees should not be omitted from future investigations. However, the study of Giometto et al. (2017) concentrated on investigating turbulence statistics and momentum transfer rates using area averages or intrinsic double averages (where temporal dimension is also averaged), which cannot convey information about the localized root causes. Furthermore, these studies considered neutrally stratified boundary layers, thus, omitting the heterogeneous thermal boundary condition of a real urban surface. The thermal aspect was considered by Yaghoobian et al. (2014), who demonstrated through an LES investigation featuring an idealized urban model how the varying thermal distribution of the surfaces alter the flow behaviour within the street-canyons. However, to what extent these conclusions are applicable within real urban environments still remains unresolved.

None of the aforementioned studies address the issue of what is the necessary level of detail (LOD) at which the urban surface (buildings, trees, thermal distribution, etc.) or the ABL flow (depth and stratification) must be described to resolve the urban flow problem of interest. Thus, this numerical sensitivity study seeks to clarify the most central LOD issues relating to urban flow modelling by performing a series of LES simulations where the LOD of the following modelling aspects are varied: (1) Surface temperature distribution, (2) leaf area density distribution, (3) ABL height, (4) inlet boundary condition and (5) LES resolution. The urban surface model features a down-town area of Helsinki, the coastal capital city of Finland, and it is processed from the latest LiDAR dataset provided by the City as open data. As an outcome, the simulations and the subsequent analysis will reveal original information that will be essential when LES solver validation is sought in a real urban setting.

METHODS

In this investigation the PArallelized Large-eddy Model, PALM (Maronga et al., 2015), is employed to run the urban LES simulations. PALM implements the non-hydrostatic, filtered, incompressible Navier-Stokes equations together with a sub-grid-scale model according to Deardorff (1980). The software is particularly well suited for the current study since it has been carefully optimized for massively parallel computing and features a nesting capability that enables a finer resolution to be utilized within the RSL.

The digital elevation model (DEM) of Helsinki with 1 m resolution is employed together with a detailed description of the street and park trees with the city (Tanhuanpää et al., 2014). Both digital models are obtained from the LiDAR dataset which is distributed as open access data by the City of Helsinki. The LES simulations will also utilize 1 m resolution within the inner nested domain (covering the relevant part of the RSL), but the surrounding outside region is resolved with 2.5 m resolution. The comparative investigation is carried out by collecting flow data at high temporal resolution over various location within the downtown area spanning from low altitude up to elevations reaching well into the Inertial Sublayer (ISL). These datasets from each simulation will be subjected to a thorough analysis, including joint time-frequency analysis with wavelets, to expose in high detail how different LOD choices influence the resolved turbulence structures, and up to which height these influences are significant.

CONCLUSIONS

The proposed computational sensitivity study of urban flow modelling will provide new and much needed information about what should be the sufficient level of detail of the urban surface model in an LES study with a given set of objectives.
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ON MEASUREMENTS AND SPATIAL DISTRIBUTION OF LIGHT ABSORBING AEROSOLS IN THE ARCTIC

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Keywords: AEROSOL LIGHT ABSORPTION, AEROSOL MEASUREMENTS, TRAJECTORY ANALYSIS, ARCTIC.

INTRODUCTION

The Arctic is particularly sensitive to changes in surface temperature and is coupled to sea ice extent (Serreze and Barry, 2011). Therefore, an increase in surface temperatures in the Arctic, through the coupling of sea ice and surface temperature, gives rise to an Arctic amplification that is driven by heat transfer from open water instead of sea ice. Arctic warming has further been exacerbated by the reduction of sulphur emissions in the northern hemisphere, thus fuelling the Arctic amplification. During the last decade, 75% of the Arctic sea ice volume has been lost and multi-year sea ice is at an all time low. Snow and sea ice are some of the most reflective (highest albedo) surfaces that occur naturally. Both pristine snow and sea ice have a very high albedo and therefore reflects the suns energy back into space. However, when light absorbing impurities are present, the albedo decreases substantially thus converting sunlight into heat. Impurities such as black carbon (BC) in snow are found throughout the Arctic and is the most potent light absorber there is. Light absorbing impurities end up in the snow and ice sheets in the through atmospheric transport and the subsequent deposition of aerosol particles. Also, the harmful climatic effect of BC and soot is not limited to deposition onto snow and ice.

The potential of BC to perturb surface temperatures in the Arctic makes measurements of BC particularly important. A widely used means to measure BC, not only in the Arctic, is by filter based absorption photometry which yields light absorption coefficients (σap) and can subsequently be converted to equivalent BC (eBC) mass concentrations. This work focuses on the light absorption photometer called the Aethalometer using a new method to improve the detection limit of this instrument. A lower detection limit is desired since BC concentrations can be low in remote areas. However, this does not imply that the concentrations are insignificant. Using the lower detection limit, a footprint is calculated using Aethalometers from six Arctic stations to estimate the spatial distribution of eBC in the Arctic.
METHODS

Aethalometers that are deployed in clean environments can seemingly be reporting just noise. An alternative method to reduce noise in Aethalometers using an filter attenuation change ΔATN threshold for boxcar averaging (Hagler et al., 2011). In this work, this same criterion from Hagler et al. 2011 is used i.e. an attenuation change (ΔATN) threshold needs to be exceeded for post-processing calculations to be invoked. Instead of using this one criterion for boxcar averaging intervals, ΔATN is used in the post-processing calculations using the modified Aethalometer equation

\[
\alpha_{ap} = \frac{1}{C_f} \frac{A \cdot \Delta ATN}{Q \Delta t \cdot 100}
\]

where \(A\) is the spot size area, \(Q\) is the flow rate, and \(\Delta t\) is the time during which ATN changes. The term \(C_f\) has been added to the Aethalometer equation and is given a value of 3.20 (Backman et al. 2016). By waiting for a ΔATN threshold to be reached in data post-processing, the relative uncertainty of the light absorption coefficients are kept constant; for non-drift situations. This results in a time series with a eBC concentration adapted time series.

Figure 1 show the concentration adapted time series and one hour boxcar averages for six Arctic stations. The stations are Alert (Canada), Summit, (Greenland), Barrow (Alaska), Tiksi (Russia), Pallas (Finland), and Zeppelin (Svalbard).

![Figure 1. Light absorption coefficients measured at six Arctic stations using Aethalometers. Boxcar averages are 1 hour averages and collection time is \(\Delta t\) in Eq. (1).](image)

Lagrangian trajectory models are widely used to in investigate source-receptor relationships of atmospheric constituents based on air-mass movement from gridded meteorological data. The method involves the calculation of an air parcels movement from the receptor site (i.e. back in time) which yields the back-trajectory of the virtual parcel of air. Individual trajectories are then matched with observed atmospheric constituents as measured at the receptor site to derive a spatial pattern on the air-mass origin in relation to the respective concentration of the constituents at the receptor site.

In this work, the air-mass back-trajectory analysis was conducted using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) version 4.9 (Stein et al., 2015). The HYSPLIT model was run using the ensemble method 7 days back in time. The ensemble method will offset the meteorological grid by one grid point in the horizontal and 1% of the surface pressure in the vertical. This
will produce 27 back-trajectories for all possible offsets in the horizontal and vertical thus accounting for uncertainties in the gridded meteorological data. The meteorological data used for the trajectories was the NCEP/GDAS dataset with a 1° horizontal resolution and 23 pressure levels (Kanamitsu, 1989). The back-trajectory analysis was done by assigning the aerosol properties as measured at the arrival time and assigning those properties to the grid cell centres that that the trajectory-path traversed. This allows for a footprint to be constructed using the measured aerosol properties at the different receptor sites as

$$C_i = \frac{\sum_{n=1}^{N} C_n W_n}{\sum_{n=1}^{N} W_n}$$

In Eq. (2), $C_i$ is the mean concentration in grid cell $i$ of the aerosol property $c_n$ weighted by $w_n$ comprising $N$ trajectory passes through the grid location $i$. Due to multiple receptor locations, the weights used were inverse distance travelled from the receptor point. Thus, the receptor location closest to a grid cell will weigh the grid cell the most which is justified since the trajectory path becomes more uncertain with greater distance travelled. This follows the rationale that station closest to a grid cell is the most representative since deposition and mixing reduces and dilutes the pollutants from a source. The aerosol properties $c_n$ investigated was $\sigma_{ap}$. Furthermore, uncertainties in the trajectory path increases with distance travelled. Figure 2 shows the footprint of the Arctic based on observational data from the six Arctic stations.

Figure 2. Footprint of light absorption coefficients ($\sigma_{ap}$) using data from the six Arctic stations at a wavelength of 700 nm. The figure comprise back-trajectories where the trajectory altitude was less than 500 metres above ground level. Red stars mark the locations of the respective stations. Latitude and longitude grid lines are spaced 15° and 30° apart, respectively. Grid cells that have fewer than 5 trajectory overpasses have been omitted.
DISCUSSION AND CONCLUSIONS

Figure 2 depicts the $\sigma_{ap}$ footprint obtained using measurements from six Arctic stations. The figure shows that during the measurement period considered, air-masses that originate from the east (i.e. from Russia) were associated with higher $\sigma_{ap}$ than those associated with air masses originating over North-America. Previous model results imply that the Russian Arctic is a substantial pathway for poleward transport of BC into the Arctic whereas North America need not be (Huang et al., 2010). In this study, the lowest $\sigma_{ap}$ could be found over an area covering southern Greenland expanding out over the ocean to the Svalbard archipelago (i.e. the Norwegian Sea).

The method used for the footprint does not include any deposition, just airmass location history. Therefore, a source region that is far away from any of the measurement stations is likely to be affected by removal processes, such as wet deposition, along the way. It remains unclear if removal processes, or the method used here, is the reason that Europe does not show up in Fig. 2 although the area should be a substantial contributor to light absorbing species in the Arctic (Koch and Hansen, 2005; Huang et al., 2010). Again, the figure should be interpreted keeping in mind that uncertainties in the method increase with distance to any of the measurements stations. Interestingly, the area east of the Caspian Sea with higher values of $\sigma_{ap}$ both showed up in the individual footprints of the stations Pallas, Alert and to some extent Tiksi.

ACKNOWLEDGEMENTS

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MEASUREMENTS OF BIOGENIC VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE BY SOLID-PHASE MICROEXTRACTION ARROW AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Keywords: BVOCs, SPME fiber, SPME Arrow, GG-MS

INTRODUCTION

Biogenic volatile organic compounds (BVOCs) play an important role in atmospheric physics and chemistry. BVOCs participate in a diversity of natural processes, including plant metabolism, communication, protection and reproduction (e.g. Peñuelas and Staudt, 2010). These compounds also participate in many photochemical reactions that lead to the production of secondary organic aerosols (SOAs) precursors (e.g. Riipinen et al., 2012). The presence of SOA influences the Earth’s radiative balance, by scattering and absorbing solar radiation (direct effect) and by acting as a cloud condensation nuclei (indirect effect) (e.g. Kulmala et al., 2004). The diversity of BVOC sources, emitted species, and their trace atmospheric concentrations call for the development of new sampling devices that can offer portability and improved sensitivity. Solid-phase microextraction (SPME) is a non-exhaustive partitioning or diffusion-controlled extractive technique that allows solvent-free sampling (Poole et al., 2017). SPME fibers have been intensively employed for collection of BVOCs. However, these fibers contain small amounts of sorbent and have limited lifetime due to their fragile nature. Alternatively, a novel SPME Arrow system offers a larger amount of sorbent and maintains the capability for thermal desorption in a standard GC injector (Helin et al., 2015, Lan et al., 2016). The coated rod can be withdrawn in a steel tube, which makes this device more robust. In this research, SPME Arrow combined with gas chromatography-mass spectrometry (GC-MS) was used for the in-situ measurement of BVOCs in the atmosphere. Conventional SPME fibers were also used for comparison purposes. Complementary laboratory tests were performed before the field campaign for the characterization of SPME-based sampling techniques and coating materials used in this work.

METHODS

BVOC measurements from ambient air were performed from 11th to 15th of August, 2017, at the Station for Measuring Ecosystem-Atmosphere Relations, SMEAR II in Hyytiälä, Finland. SPME fibers coated with PDMS/DVB (65 µm, Torion Technologies Inc., Utah, USA) and PDMS/PDMS/Carbon WR (95 µm, CTC Analytics AG, Zwingen, Switzerland), and SPME Arrows coated with the same PDMS/Carbon WR (120 µm) and PDMS/DVB (120 µm) type of sorbents (CTC Analytics AG, Zwingen, Switzerland) were used for analyte collection in static mode. The SPME fibers had a sorbent length of 10 mm, while Arrows sorbent length was 20 mm. The diameter of Arrow needle was 1.1 mm. A home-made dynamic sampling system for SPME Arrow was also used for comparison with static SPME collection. This device was adapted and modified from the sampling system developed in previous research for SPME fibers (Barreira et al., 2015). Sampling time of 45 min was used in the field experiments. Samples were measured using a conventional GC-MS, consisting of an Agilent 6890 N gas chromatograph equipped with an Agilent 5973 mass selective detector (Agilent Technologies, Palo Alto, USA). The analytical column was a HP-5MS
The initial oven temperature was 70°C (1 min), and it was increased to 250°C (1 min) at 20°C/min. The total run time was 11 minutes. Helium (99.996%, AGA, Espoo, Finland) was used as carrier gas in a constant flow mode (1.5 mL/min). SPME Arrow and fibers were desorbed in splitless mode (2 min) with a 2.0 mm internal diameter (i.d.) split/splitless inlet liner. Desorption temperature was 270°C for all SPME devices. A standard inlet septum was used for SPME Arrow, while a 23-gauge Merlin Microseal and a Merlin nut (Merlin Instrument Company, Half Moon Bay, USA) were used in the injection port for conventional SPME fibers. The temperature of GC-MS transfer line was 250°C and the ion source and quadrupole temperatures were kept at 230°C and 150°C, respectively. Electron ionization (70 eV) was used. The scan mass range was from 30–400 amu. The mass spectra and retention times of each analyte were obtained with standard solutions and used for identification of studied compounds in the collected samples. For semi-quantitation, extracted ion chromatograms with base ions were used (m/z 93 for α-pinene, Δ3-carene and limonene; m/z 43 for octanal and decanal; and m/z 57 for nonanal).

The method used for the laboratory tests was similar to the one employed for the field measurements, although the initial oven temperature was 50°C (1 min) and the final temperature 250°C (1 min) at 20°C/min. For the laboratory determination of analytes extraction time profiles and to compare the extraction efficiencies of the different SPME-based sampling techniques, an Agilent 5975 C mass selective detector (Agilent Technologies, Palo Alto, USA) was used, while all other laboratory tests were performed with the same GC-MS used for the field measurements. In the laboratory tests, samples were collected during 10 minutes, except for studying the effects of temperature and relative humidity on the collection of BVOCs in which a 20 minutes sampling time was chosen.

![Figure 1. Comparison between the mass of identified monoterpenes (α-pinene, Δ3-carene and limonene) and aldehydes (octanal, nonanal and decanal) collected with different SPME Arrows (PMDS/DVB and PDMS/Carbon WR) from ambient air and measured by GC-MS (submitted to Atmospheric Measurement Techniques).](image)

**CONCLUSIONS**

A novel SPME Arrow system was successfully employed for the collection of BVOCs from ambient air. Samples were collected and analyzed by SPME Arrow and fiber devices and conventional GC-MS. Neither additional sampling line nor sample pre-treatment was needed, reducing analysis time, sample contamination and potential losses. The most abundant monoterpenes and aldehydes were measured with both SPME systems used (Figs. 1 and 2). PDMS/Carbon WR had higher affinity towards Δ3-carene and limonene than PDMS/DVB, while PDMS/DVB enhanced the extraction of α-pinene. Nonanal and decanal were the most abundant aliphatic aldehydes. The extraction efficiency of the SPME Arrow was two times higher than of SPME fiber, with exception for aldehydes during the field campaign where a 7-fold extraction enhancement was observed. Results were in agreement with the meteorological parameters that influence the atmospheric amounts of BVOCs in the atmosphere. However, laboratory tests showed that
an increase in temperature and relative humidity causes a decrease in the extracted amounts of BVOCs, especially when PDMS/Carbon WR is used (Figs. 3 and 4). Overall, results demonstrated the benefits and challenges of employing SPME Arrow for the in-situ measurement of BVOCs in the atmosphere. More studies under controlled conditions are needed to understand the influence of co-adsorbed species and to develop a proper calibration method for field measurements.

Figure 2. Comparison between the mass of identified monoterpenes (α-pinene, Δ3-carene and limonene) and aldehydes (octanal, nonanal and decanal) collected with different PDMS/DVB coated SPME devices (fiber and Arrow) from ambient air and measured by GC-MS (submitted to Atmospheric Measurement Techniques).

Figure 3. Effect of temperature (°C) on the extraction efficiencies obtained with SPME ARROW using Carbon WR and PDMS/DVB sorbents (submitted to Atmospheric Measurement Techniques).

Figure 4. Effect of relative humidity (%) on the extraction efficiencies obtained with SPME ARROW using with Carbon WR and PDMS/DVB sorbents (submitted to Atmospheric Measurement Techniques).
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VERTICAL PROFILE OF AIRBORNE MEASURED ION COMPOSITION ABOVE THE BOREAL FOREST

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Keywords: Airborne Measurement, Mass Spectrometry, APi-TOF, Ion Composition, Ion Concentration, New Particle Formation.

INTRODUCTION

New particle formation (NPF) is an important source of aerosols with climatically relevance. It is investigated since 1995, for example, in the SMEAR II station at Hyytiälä, Finland (Kulmala et al., 2001, Kulmala et al., 2004, Kulmala et al., 2013). In order to better understand the processes involved in NPF, and compile comprehensive observations of the vertical distribution of particles, clusters and ions, an airborne measurement campaign above the SMEAR II station and its surroundings between the 28th of April and 16th of May 2017 was performed. For the measurements, two Cessna 172 were equipped with several aerosol instruments as well as an APi-TOF. The aim of the campaign was the measurement of the particle distribution as well as the ion concentration and composition within and above the boundary layer. In the last few years several campaigns have been made using small aircrafts to investigate new particle formation above the boreal forest (Laaksonen et al., 2008, O’Dowd et al., 2009, Schobesberger et al., 2013, Väänänen et al., 2016).

METHODS

For the campaign two small aircrafts, Cessna 172, were equipped with instruments for aerosol and ion measurements. The first aircraft was equipped with an Atmospheric Pressure interface Time of Flight (APi-TOF), measuring the ion composition, a temperature and humidity sensor as well as a GPS tracker. The second aircraft was equipped with a Condensation Particle Counter (CPC), a Scanning Mobility Particle Sizer (SMPS) and a Particle Size Magnifier (PSM). Furthermore, meteorological parameters were monitored with a wind profiler, temperature and humidity sensor and a GPS tracker. After 70% of the flight hours, the instrumentation was changed to a Neutral cluster and Air Ion Spectrometer (NAIS) to measure the ion-cluster concentration ranging from 1 to 40 nm in diameter-size. In order to run the instruments autonomously during the flight, a battery system for each aircraft was built. Furthermore, a moving inlet system was constructed to keep the inlet for the air sample inside the aircraft during take-off and landing. For the APi-TOF measurement several additional equipment were added: an x-ray source was used every 10 min for 20 seconds to examine if a signal was measured. The x-ray data were not used for further data analysis. In order to insure a stable pressure inside the mass spectrometer, a pressure controller was attached to the first chamber of the instrument. Also, the mass flow was adjusted to the ambient pressure, enabling a constant volumetric flow during the measurement.

The altitude profiling was made by three different layers at a height of 300 m, 1000 m and 3000 m. At each altitude level, a 10-minute leg above Hyytiälä was flown (see figure 1 and 2). The flight route (figure 2) departed at the Pirkkala Tampere airport, about 50 km linear distance apart from Hyytiälä. In total 16 flights were operated, whereas one flight lasted 2.5 hours. Both aircrafts flew in a row, the first one was the APi-TOF airplane. The aerosol measurements were taken several meters behind the APi-TOF airplane at a higher altitude on the right side avoiding to contaminate the air sample through the exhaust of the first
plane. The flying days took place during fair weather conditions and possible NPF-days in Hyytiälä. For investigating the development of the boundary layer and the vertical mixing during the day, two to three flights per day were flown. The early morning flights were proceeded from 3:00 to 5:30 (EET), the morning flights from 8:00 to 10:30 (EET) and the midday flights between 13:30 – 16:00 (EET).

Figure 1: Vertical flying profile over Hyytiälä, Finland
Figure 2: Flight route from the airport Pirkkala Tampere to Hyytiälä

OUTLOOK

In further data analysis, the airborne data will be analyzed in regard to the ground based measurements, and the data from the 35-m tower in Hyytiälä station. Furthermore, the aerosol measurements will be compared with the ion composition, especially regarding the NPF events. The vertical profile and the behavior of the ion distribution based on the boundary layer and their diurnal variation will be examined and analyzed.

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IMPLICATIONS OF MYCORRHIZA, INSIGHTS FROM A THEORETICAL MODEL

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Keywords: Decomposition, Priming, Mycorrhiza

INTRODUCTION

Soil ecosystems are locations where the fate of plants and diverse decomposer communities are intertwined. Litter from plants is fed to mycorrhiza, saprophytic fungi or soil bacteria to make nutrients available to plants which then again produce litter. Litter quality on the other hand largely determines which microorganisms decompose soil organic matter. This shows a network of complex interactions where both plants and decomposers interact through competition and mutualistic interactions. This leads to two sorts of interrelated questions: (1) How do the different functional types coexist under varying environmental conditions and (2) what are the implications of the composition of the decomposer community for nutrient cycling and ultimately plant productivity.

While traditional biogeochemical decomposition models like RothC or Century do not simulate explicitly decomposers new models that are based on microbes and their activity are evolving. These new biogeochemical models, that are based on enzyme activity simulate biogeochemical cycling explicitly based on the activity of decomposers, their stoichiometry and their activity (Schimel and Weintraub 2003). Waring et al. (2014) showed that the approach could be extended to simulate the coexistence of functional groups during litter decomposition. Similarly, market perspective based approaches which, however, lack the population dynamics of decomposers of the enzyme based models, have been successfully applied to analyze nutritional gradients. However, empirical data showed conflicting results on the benefits of mycorrhiza on plant nutrition and growth, which puts forward the question why do plants invest up to 30\% of their productivity into mycorrhiza.

METHODS

We modified the decomposition model Schimel and Weintraub (2003) following the ideas of Waring et al. (2014) to include different functional groups of decomposers as well as adding plant production to the model.

The Schimel and Weintraub model is a model that simulates litter decomposition as a function of enzyme activity and decomposer stoichiometry. The model assumes that the stoichiometry of decomposers is fixed (strong homeoeostasis). Decomposers produce exo-enzymes that degrade soil organic matter and produce dissolved organic matter. Decomposers take up the dissolved organic matter for growth and respiration and decompose soil organic matter using exoenzymes. Excess carbon is respired using overflow respiration while excess nitrogen is mineralized. Ammonium and nitrate are not modeled explicitly and...
no transformations of inorganic nitrogen as Nitrification are modeled. Microbes may also acquire nitrogen via immobilization.

Our modification of the model was to divide the decomposer pool into saprophytic fungi, mycorrhizal fungi and bacteria. These functional groups have different C/N ratios as modeled previously by Waring et al. (2014). In difference to their paper we assumed that microbial DOC uptake is proportional to the the share of each functional group in biomass and the activity of the functional group, while Waring et al. (2014) assumed it to be proportional the share of the enzyme production of each functional group. In addition mycorrhizal fungi receive a fixed share of the net primary production of the plant while they return a fixed proportion of their nitrogen uptake to the plant (see equations Xx and xx in the appendix).

Plant net primary production (including growth allocated to mycorrhiza) was assumed to be proportional to the plant nitrogen uptake and ratio of plant production and nitrogen uptake equalled the C/N ratio of the litter. We defined two different plant functional groups (mycorrhizal and non-mycorrhizal plants). Plant senescence was assumed to be a fixed proportion of plant biomass and this biomass was returned to the soil as litter. Both mycorrhizal and non-mycorrhizal plants take up soil inorganic nitrogen as a fixed proportion of the inorganic nitrogen stock. Mycorrhizal plants receive, in addition, a fixed proportion of the nitrogen taken up by mycorrhiza and that is used for growth.

RESULTS

The resuls of the simulation experiment (Figures 1) indicate that the presence of mycorrhiza did not increase the plant biomass or soil organic carbon. In the model with competition between mycorrhizal and non-mycorrhizal plants mycorrhizal plants dominated the ecosystem towards the end of the ecosystem development. However, the microbial biomass was higher in the presence of mycorrhiza, while N mineralization rates as well as the inorganic nitrogen were higher in the absence of mycorrhiza. For the simulation with mycorrhizal plants the acquisition of N via mycorrhiza was equal to the acquisition via uptake of inorganic nitrogen (both values were 0.016 g N m⁻² day). Mycorrhiza dominated the microbial biomass at the end of the simulations with over 85% of the total microbial biomass while the uptake of N occurred almost uniquely via the mycorrhiza.
We also explored the effect of changes in the proportion of mycorrhizal N uptake that is allocated to the plant. If little N is transferred from the plant to the mycorrhiza (but mycorrhiza still receive substrate from the plant) the mycorrhizal biomass is high and displaces all other soil decomposers while mycorrhizal plants are less frequent. Higher levels of transfer of N from the mycorrhiza to the plant decrease mycorrhizal biomass and the biomass of bacteria and saprophytic fungi increases. Inorganic N decreases strongly when N allocation to the plant decreases and then settles at low level. Mineralization of N first decreases with an increasing proportion of N allocated to the plant but then increases again. The point of the increase coincides with the point where saprophytic fungi and bacteria are gaining importance. Surprisingly there were little effects of the allocation of N to the plant on plant biomass and soil carbon (variation in both variables was less then 5%).

**DISCUSSION**

Our model allows for a realistic description of the general patterns of ecosystem development and mycorrhizal biomass reacts, somehow realistically to different ecological gradients. Interestingly, presence of mycorrhiza led usually to reductions in N-mineralizations because transfer of N from the fungi to the trees kept microbial biomass N -limited. These reductions of mineralization and inorganic N allowed mycorrhizal plants to dominate ecosystems since less N was available for hypothetical non-mycorrhizal plants.

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WHAT IS THE MECHANISM BEHIND NEW PARTICLE FORMATION IN HIGHLY POLLUTED URBAN ENVIRONMENTS?

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Keywords: Nucleation, Mass spectrometry, Megacity, Sulphuric acid.

INTRODUCTION

A significant fraction (>50%) of cloud condensation nuclei (CCN) in the atmosphere arises from new-particle formation (Merikanto et al., 2009; Yu and Hallar, 2014). While particle nucleation has been observed almost everywhere in the atmosphere (Zhang et al., 2012; Bianchi et al., 2016), the mechanisms governing this process are still poorly understood and subject of ongoing researches (Kulmala et al., 2013; Zhang et al., 2012). One of the main goals is to elucidate the factors and underlying the mechanisms governing the initial formation of molecular clusters and particles smaller than 2 nm diameter. Recently, several achievements have been reached regarding our understanding of nucleation; however, it is still unclear why NPF occurs more often than predicted in highly-polluted conditions, such as in Chinese megacities. A recent study has shown that this apparent discrepancy can be explained only if the molecular clusters are scavenged considerably less effectively than one would expect based on their collision rates with the pre-existing particles, or if they grow much faster in size than our current understanding allows (Kulmala et al., 2017).

In general, it is still largely unknown which components participate in new-particle formation. The only compound that certainly plays a major role is sulfuric acid (H₂SO₄) (Kirkby et al., 2011; Riipinen et al., 2012). Other compounds are thus required to contribute to new-particle formation by stabilizing H₂SO₄ molecules during the initial cluster formation. Laboratory experiments and quantum chemical calculations have identified potential candidates that may play this role, including ions (Kirkby et al., 2011), ammonia (NH₃) (Kirkby et al., 2011), amines (Almeida et al., 2013; Bianchi et al., 2014), and a possibly wide range of oxygenated organic molecules (Ehn et al., 2014; Riccobono et al., 2014). In addition to that, recent studies have shown that nucleation of pure highly oxidised molecules (HOMs) without sulphuric acid is possible (Bianchi et al., 2016; Kirkby et al., 2016; Tröstl et al., 2016).

Despite the large effort in understanding new particle formation in megacities (Xiao et al., 2015; Kulmala et al., 2017), none of the previous studies have measured the chemical composition of the growing clusters. Therefore, while these studies confirm that new-particle formation in megacities is very important, they are insufficient to allow for a reasonable evaluation of the mechanisms in order to improve the accuracy of new-particle formation. A detailed framework that unifies the particles 'physical properties and the vapours' chemical composition is required to understand from first principles the fundamental pathways by which new-particle formation occurs in the atmosphere. The new instrumental
advances present a unique opportunity to determine the chemical ingredients responsible for nucleation and cluster growth in the free troposphere.

METHODS

To improve our understanding in urban NPF, we performed a comprehensive measurement campaign in Shanghai, China, from December 2015 until February 2016. The set of instruments that used in this “short” and intensive campaign are reported in Table 1. The results of this intensive campaign have been coupled with long-term measurements of PSM, Nano- and Long-SMPS (March 2014 - March 2016).

<table>
<thead>
<tr>
<th>Device</th>
<th>Measured property</th>
</tr>
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<tbody>
<tr>
<td>Atmospheric Pressure interface Time-Of-Light mass spectrometers (API-TOF)</td>
<td>Chemical composition of the positive and negative ions ($D &lt; 2\text{nm}$)</td>
</tr>
<tr>
<td>Chemical ionization-API-TOF (CI-API-TOF, NO$_3^-$ chemistry)</td>
<td>Sulphuric acid and HOM concentration and neutral clusters chemical composition ($D &lt; 2\text{nm}$)</td>
</tr>
<tr>
<td>Neutral and Air Ion Spectrometer (NAIS)</td>
<td>Particle and ion size distribution from $D = 0.4$ to $40\text{ nm}$</td>
</tr>
<tr>
<td>Nano-Scanning Mobility Particle Sizer (Nano-SMPS)</td>
<td>Particle size distribution from $D = 4$ to $100\text{ nm}$</td>
</tr>
<tr>
<td>Condensation Particle Counter (CPC)</td>
<td>Particles number concentration ($D &gt;2.5\text{ nm}$)</td>
</tr>
<tr>
<td>Particle Size Magnifier (PSM)</td>
<td>Particle number concentration ($D &gt;1\text{ nm}$) and growth rate between $D = 1$ and $2.3\text{ nm}$</td>
</tr>
</tbody>
</table>

Table 1. Instruments used at the Fudan University in Shanghai, China during the intensive campaign (December 2015 – February 2016)

While the CI-API-TOF measured the H$_2$SO$_4$ and HOM concentrations during the nucleation events, the API-TOF retrieved the chemical composition of the positive and negative ions. The ions and particle size distribution were measured with an NAIS and SMPS, respectively. As particle counters a CPC with a lower cut off diameter of $2.5\text{ nm}$ and a PSM were used. PSM measures particles with a cut off that varied from 1–4 nm (charged ammonium sulphate equivalent diameter).

CONCLUSIONS

We observed several NPF events taking place during sunny and relatively “clean” conditions. During the NPF event days, PM$_{2.5}$ was on average lower than during non-event days, although with a concentration still higher than 50 $\mu$g/m$^3$. A high concentration ($\sim 10^5$ cm$^{-3}$) of sub-3nm particles was detected with the PSM during the nucleation event. Thereafter, larger particles (4-63nm) were detected by the Nano-SMPS and the NAIS.

To complement the particle data, the mass spectrometer was able to determine the sulphuric acid and HOMs concentration during such events. Our results indicate that NPF in Shanghai is initially driven by sulphuric acid and amines followed by the condensational growth of anthropogenic HOMs.

Figure 1 shows an example of a NPF event measured at Fudan University in Shanghai. It is clear from the figure that a large number of particles ($\sim 2\times 10^4$ cm$^{-3}$) can easily reach a size of 50-60 nm in just a few hours.
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THE EFFECT OF RELATIVE HUMIDITY AND CHEMICAL COMPOSITION ON THE 
EVAPORATION OF SECONDARY ORGANIC AEROSOL PARTICLES


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Keywords: evaporation, volatility, secondary organic aerosol, chemical composition.

INTRODUCTION

Secondary Organic Aerosol (SOA) is a major constituent of atmospheric aerosol. SOA consists of a multitude of organic compounds with a wide range of physical and chemical properties, such as viscosity and volatility (Hallquist et. al., 2009). The volatility and concentration of a compound will determine its partitioning between particle and gas phase. One approach to characterize the composition of SOA particles is the Volatility Basis Set (VBS) model (Donahue et al. 2006) where compounds are grouped by their saturation concentration. Typically, VBS distributions are derived from particle growth experiments in smog chambers, and can then be used to predict various SOA properties, including the rate of evaporation of SOA particles upon dilution of aerosol with clean air. Previous studies have shown that the evaporation of a-pinene ozonolysis SOA particles in the presence of an irreversible sink for organic vapors is slower than expected from their VBS distributions (Vaden et al. 2011). The observations were explained by hindered diffusion of SOA compounds within the particles, consistent with the observation that a-pinene ozonolysis SOA particles are amorphous solids (Virtanen et al. 2010).

Another way to study the volatility of SOA compounds is to track the equilibrium particle size as well as composition as a function of temperature. These experiments are typically carried out with thermo-denuders. However, thermal decomposition of complex organic compounds at the elevated temperatures in the thermo-denuder and the possibility of accelerated chemical reactions occurring in heated particles complicates the interpretation of the thermo-denuder experiments.

We studied the evaporation behavior of SOA particles produced from a-pinene and complex VOC mixtures at different oxidation levels. Unlike studies with thermo-denuders we investigated the evaporation of the particles at room temperature in a residence time chamber (RTC) therefore eliminating thermal decomposition artifacts. We also investigated the impact of relative humidity (RH) on the particle evaporation.

Besides the physical mass transfer limitations in (semi)solid particles, there may also be chemical processes at work in the particle phase, e.g., oligomerization reactions, decreasing the rate of evaporation of the particles. Thus, studying the changes of the chemical composition of particles during evaporation may provide further insights into the processes governing the particle evaporation kinetics. We applied...
two complementary methods: Aerosol Mass Spectrometry, which provides an average atomic composition of SOA particles, and a Filter Inlet for Gases and AEROsols (FIGAERO) coupled with Chemical Ionization Time-of-Flight Mass Spectrometer (CIMS) which provides information on molecular composition as well as volatility of the compounds.

METHODS

An Aerodyne Potential Aerosol Mass (PAM) oxidation flow reactor (Lambe et al., 2011) was used to produce SOA with a range of compositions via photooxidation of a-pinene or a complex mixture of VOCs. For all experiments, the basic conditions in PAM were constant (residence time, RH, temperature, initial VOC concentration). The integrated oxidant exposure inside the reactor was manipulated by varying the UV light intensity, thereby allowing the generation of SOA with O:C ratios ranging from 0.55 – 1.05. A Nano-Differential Mobility Analyzer (NanoDMA 3085, TSI Inc.) was used to select a quasi-monodisperse particle distribution at 80nm. The NanoDMA also removed the majority of gas phase compounds due to the extremely short residence time and the open loop configuration of the sheath flow (dilution factor ~100). The changes in particle size and composition were measured with a set of instruments (see below). The length of the tubing leading to these instruments was varied to achieve evaporation times between 4 and 150 sec. To investigate evaporation times up to 10 h, the monodisperse aerosol was flushed into the 100 L stainless steel residence time chamber (RTC) and then the RTC was closed off from all air flows. The content was sampled briefly in ~1 h intervals replacing the sampled volume with clean air. The stainless steel surfaces of the tubes and the RTC acted as an irreversible sink for the vapors evaporating off the particles, as confirmed by the insensitivity of the observed particle evaporation rates to the initial particle concentrations in the system for the investigated particle concentration range. A second set of experiments was conducted with longer RTC filling times in order to reach the higher aerosol mass concentrations needed for FIGAERO measurements. Two to three hours after ending the filling, the content of the RTC was sampled onto the FIGAERO filter and analyzed.

For the humid experiments (RH 40% & 80%), the RH of the system was controlled by humidifying the sheath flow of the size selection NanoDMA while maintain constant humidity inside the PAM reactor. The RTC was flushed with air of the target RH prior to the experiments.

The VOC concentration on the inlet of the PAM was measured with a Proton Transfer Reaction time-of-flight Mass Spectrometer (PTRMS, Ionicon).

The chemical composition of the SOA particles was investigated with a High Resolution time-of-flight Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc.) and a Filter Inlet for Gases and AEROsols (FIGAERO, Aerodyne Research Inc., Lopez-Hilfiker et. al., 2014) coupled with Chemical Ionization Time-of-Flight Mass Spectrometer (ToF-CIMS, Aerodyne Research Inc. and Tofwerk AG) using iodide-adduct ionization (Lee et. al., 2014). The size distribution of the particles was measured with a Scanning Mobility Particle Sizer (SMPS, TSI Inc.).

Figure 1: Schematic diagram of the experimental set-up and fate of aerosol particles.
RESULTS AND DISCUSSION

The evaporation of the particles is expressed as evaporation factor (EF) which is the ratio of the measured particle diameter ($D_p$) and the selected particle size ($D_p(set)$). The evapograms of the low O:C ratio a-pinene experiments are shown in Fig. 2. Particles evaporated already during the short passage from the NanoDMA to the SMPS (up to 5% reduction of particle diameter). After further fast evaporation during the first ~30 min in the RTC, the diameter continued to decrease slowly as the particles sat in the RTC for several hours.

Particles showed considerably more evaporation under humid conditions in the RTC compared to dry conditions which is consistent with observations of Wilson *et al* (2015) and Yli-Juuti *et al.* (2017) for SOA particles from ozonolysis of a-pinene. There are two likely explanations: Water acts as a plasticizer, thus reducing mass transport limitations in the humidified particles compared to the (semi)solid dry particles, or water can play a more active chemical role for example by hydrolysis of less volatile dimers resulting in more volatile monomers in the particle phase. The detailed FIGAERO mass spectra will help investigating these two possibilities.

Although the particle evaporation considerably reduced the particle size, the O:C ratio measured by the AMS was stable throughout each evaporation experiment. But there was a clear dependence of the observed evaporation rate on the initial chemical composition of the SOA, as expressed by the O:C ratio, with volatility and the evaporation rate increasing with decreasing O:C ratio.

Figure 2: Evapograms (evaporation factor vs residence time) for low O:C a-pinene experiments.
The FIGAERO thermograms (Figure 3) showed a shift to higher evaporation temperatures for SOA that has aged in the RTC compared to fresh SOA, i.e. the residual particles are less volatile. Similar to the AMS data, there is almost no change in the average O:C ratio with evaporation. Using the mass spectra data we can define compounds with 10 or less C atoms as “monomers” which are most probably more volatile and anything with more C atoms as “dimers” which are most likely less volatile. With this definition, we find a shift in the monomer:dimer ratio towards dimers with evaporation. I.e. the more volatile “monomers” leave the particles and most “dimers” remain. Assuming that monomers and the corresponding dimers have a very similar O:C ratio, this can explain the almost constant O:C ratio during evaporation and at the same time strong dependence of evaporation on the initial SOA O:C ratio.

The results of this study have several important implications. Biogenic SOA particles can be transported over long distances from the point of their formation. They are slowly oxidized during the transport, and become more resistant to evaporation during dilution of the transported air mass. Furthermore, the transported air mass can experience changes in temperature and relative humidity, both of which affect the particle evaporation rates. The hindered evaporation may increase climate effect of SOA relative to what would be predicted by an equilibrium gas-particle partitioning model.

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VERTICAL ION DISTRIBUTION: EFFECT OF FOREST CANOPY AS AN ION SINK

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Keywords: ions, canopy, vertical distribution, deposition.

INTRODUCTION

Radiation (such as Rn and cosmic rays) ionises air molecules that can then cluster with other air molecules and potentially lead on to new particle formation (Hirsikko et al., 2007, Laakso et al., 2004). Ambient conditions observed in Hyytiälä SMEAR II station, Finland where simulated within the CLOUD chamber experiment. A comparison with observations highlighted a possibly larger role played by ions in new particle formation than expected (Wagner et al. submitted). In this study we investigate the vertical distribution of ions in a boreal forest canopy in order to account for any underestimation of the sink of ions due to the forest canopy. The results are aimed to further evaluate the role of small ions in new particle formation.

METHODS

We are investigating the diurnal variations in ion concentrations at two heights in a boreal forest: from ground to above canopy height (35 m). Specifically, we are evaluating the extent of the forest canopy as an ion sink. Measurements are taken from the boreal forest site SMEAR II, in southern Finland (61°52’N, 24°17’E), considered to be a background site. Two Neutral Air Ion Spectrometer (NAIS) have been operating almost continuously at ground level (inlet: 4 m height) and above canopy level (35 m tower) since 2014. Additionally, a side-to-side comparison of the instruments has been carried out during this time period in order to evaluate the precision of the instruments and account for instrumental internal errors. As a supplement, long-term (2003 until present) ion measurements from a Balancing Scanning Mobility Analyser (BSMA) are available at ground level to act as a reference for ion concentrations. Radon concentration measurements at the station are only available at ground level, so a direct measurement of ionisation is not available, and ion concentration is based only on the aerosol size distribution data (NAIS). Given that the forest floor is a source of radon, we expect ion concentrations at ground level to be higher compared to above-canopy (Tammet et al., 2006). We also investigate meteorological conditions such as fog days, in order to investigate the periods when the small ions (<2 nm) concentration momentarily decreases (or disappears) in the above-canopy measurements but not at ground level.

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REFERENCES


ION MOBILITY SPECTROMETER (IMS) COUPLED WITH A TIME OF FLIGHT MASS SPECTROMETER FOR HIGH-RESOLUTION AMBIENT GAS AND AEROSOL ANALYSIS

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Keywords: IMS, MS, CI-APITOF

INTRODUCTION

The aim of this research is to investigate the viability of utilising mobility spectra from IMS coupled to a ApiTOF (atmospheric pressure interface time of flight mass spectrometer) for chemical composition analysis of cluster ions using electrospray-ionisation (ESI) for ambient data from Hyytiälä, Finland, and utilising calibration from known mobility sample chemicals.

In ESI, a small liquid flow is nebulised into an aerosol through a capillary tube that is placed at high potential and provided a stream of an inert gas or air at the needle tip. Ions formed from an analyte molecules may be multiply charged. When entering the drift tube the formed ions encounter hot gas, which assists in the desolvation of the droplets. The solvent evaporates from a charged droplet until it becomes unstable upon reaching its Rayleigh limit. At this point, the droplet deformes as the electrostatic repulsion of like charges, in an ever-decreasing droplet size, becomes more powerful than the surface tension holding the droplet together. At that point the droplet undergoes Coulomb fission, whereby the original droplet 'explodes' creating many smaller, more stable droplets. The new droplets undergo desolvation and subsequently further Coulomb fissions, creating ions of known composition.

ESI is a so-called 'soft ionisation' technique, since there is very little fragmentation. This can be advantageous in the sense that the molecular ion is always observed, however very little structural information can be gained from the simple mass spectrum obtained. This disadvantage can be overcome by coupling ESI with tandem mass spectrometry (ESI-MS/MS), as has been done for this experiment. Another important advantage of ESI is that solution-phase information can be retained into the gas-phase.

IMS is built upon the principle of ion movement in the presence of a stable electrical field. The drift time, $t_d$, is proportional to its electrical mobility, $K$, and dependent on the temperature and pressure of the drift tube.

IMS separates ions in gas phase based on this property $K$, which is sensitive to the shape and mass of the ion as well as ion-chemical interactions with the ambient air or buffer gas. To account for the temperature and pressure dependencies, as well the electrical field, it is common to use $K_0$, the reduced mobility, which is normalised to base pressure and temperature and applied electric field potential $V$.

As IMS is based on electrical mobility and not polarity, it is not limited by solvent or column constraints, as are Liquid Chromatography (LC) or Gas Chromatography (GC). IMS offers species’ separation of isomeric and isobaric compounds that would otherwise be not possible with LC or GC.

This fact has led IMS to be utilised in various applications, such as chemical agent, drug and explosives detection, medical uses as in protein, peptide and amino acid analysis and also Volatile Organic Compounds (VOCs) detection (Eiceman et al. 2013).
The CI-APi-TOF instrument consists of three main components: a chemical ionisation inlet (CI), an atmospheric pressure interface (APi) and a time-of-flight mass spectrometer (TOF) (Jokinen et al., 2012). The APiTOF is described extensively in (Junninen et al. 2010). The atmospheric pressure interface (APi) guides the sampled ions in atmospheric pressure to a time-of-flight mass spectrometer (TOF). Three chambers, each containing a turbo pump, differentially pressurise the chambers.

IMS separates on the millisecond timescale and thus couples well with time-of-flight (TOF; IMS-TOF) mass spectrometry, which operates on a microsecond timescale (Krechmer et al. 2016). IMS-TOF instruments can acquire multiple mass spectra for each ion mobility spectrum data point (Kanu et al., 2008).

**METHODS**

An Ion Mobility Spectrometer (IMS) is coupled to a APiTOF with Electrospray-Ionisation (ESI) in the initial stage.

The location from which our data has been collected is the Station for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR II) station located in the boreal forest site in Hyytiälä, Southern Finland (61°51’N, 24°17’E, 181 a.s.l, Hari and Kulmala, 2005).

For the calibration using tetra-alkyl-ammonium halides, (Ude & de la Mora, 2005) and (Viidanoja et al. 2005) provide reference reduced mobilities in air using ESI for many tetra-alkyl-ammonium halides.

A single calibrated theoretical length for the drift region was attempted based on utilising literature reduced mobility values.

The effective length of the drift region is different from the true physical length of the drift tube, due to the electrophysics present in the instrumental setup. Main factors that deviating effective length and true length of the drift tube are electrical field around IMS entrance gate and the time spent by ions in APi region of the APiTOF. Therefore, calculating an average effective length of the drift region based on literature reduced mobility values is used as calibration. The calibration compounds include THAB (tetrabutyl ammonium bromide, m/z=242), TDDAB (tetra-dodecyl ammonium bromide, m/z=691), EMIBF4 (1-ethyl-3-methylimidazolium tetrafluoroborate, m/z=111) and TBAB (tetrabutyl ammonium bromide, m/z=242). The calibration was repeated for different electrical voltage applied, U, and two different temperature values T, 60 degrees Celsius and 80 degrees Celsius.

The results of the calibration can be seen in Fig. 1. All monomers and one dimer (THAB, m/z=886) are shown for different electrical voltage U applied, and in most cases for two different temperatures.

At higher temperature, it is possible there is some clustering from water vapour molecules at 80 degrees Celsius, explaining the generally lower effective length of the drift region at that temperature. Apart from the only dimer in the calibration setup (the THAB dimer m/z=886), the length exhibits a minimum for varying electrical field applied, U. The cause of this is still unclear, though length is theoretically related to U by a squared relationship.

The objective of the calibration was to find a single factor to modify, to be as close as possible to the calculated literature reduced mobility values. By simply taking the mean of these theoretical lengths at T=333K, discarding the T=353K values due to possible contamination clustering, we found L=19 cm to calibrate our setup.
CONCLUSIONS

Figure 1: Calibration using tetra-alky-ammonium halides. The theoretical length of the drift region was calculated from literature reduced mobility values. Based on the lower temperature data (333K) an average for the length was determined to be 19 cm.

Figure 2. Mass-to-charge (m/z) vs reduced mobility $K_0$. Low IMS response signal (<150 arbitrary units) was filtered out. The density curves for 0.5 – 1.0 g/cm$^3$ are also shown.

Reduced mobilities, $K_0$, were calculated for all compounds, based on maximum IMS response for a given m/z. In addition, assuming spherical particles, the bulk density of clusters was computed, as seen in Figure 2.
Figure 3. Reduced mobility $K_0$ vs. mass-to-charge ratio $m/z$. Compounds with the same reduced mobility are linked with a line and are likely to be part of the same cluster when entering IMS. This analysis could potentially be used to identify how e.g. compound $m/z=339$ clusters on event days vs non-event days.

The instrument setup yielded valuable cluster-level information in addition to normal MS measurement data, as seen in Figure 3.

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REFERENCES

OBSERVATIONS OF OZONE DEPLETION EVENTS AT SMEAR II STATION IN A FINNISH BOREAL FOREST

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Keywords: Ozone depletion, boreal forest, long-term observation, case study.

INTRODUCTION

Ozone plays an important role in atmospheric chemistry. In stratosphere, it attenuates detrimental ultraviolet radiation, but it is usually considered as a pollutant in troposphere (Monks et al., 2015). Being one of the major natural oxidants present in the atmosphere, ozone can cause oxidative damages to plant surfaces as well as to human respiratory system (Emerson et al., 2001; Turner et al., 2016). Ozone also acts as a greenhouse gas that contributes to global warming in the lower atmosphere. (Monks et al., 2015). In addition to the direct climatic effect, ozone influences climate via aerosol formation and the subsequent cloud formation. Recent studies suggested the autoxidation mechanism of volatile organic compounds (VOCs) by ozone forming highly oxidised multifunctional compounds (HOMs) (Ehn et al., 2014; Rissanen et al., 2014). These HOMs likely participate in atmospheric new particle formation and growth (Trostl et al., 2016). Therefore, it is crucial to monitor atmospheric ozone concentrations. One of the major anomaly in the variation of ozone concentrations is the infamous ozone hole in polar stratosphere attributed to the depletion of ozone by the catalytic halogen chemistry (Molina and Rowland, 1974; Solomon, 1999). Ozone depletion has also been reported in surface ozone in polar planetary boundary layer (Simpson et al., 2007) and in polluted urban environments (Gregg et al., 2003). The reasons come either from halogenated destruction or from complex chemistry involving anthropogenic emissions. These observations of surface ozone depletion were often reported with the lack of the vertical profile information on ozone concentrations. In this study, we analysed a 20-year-long ozone dataset collected between 1996 and 2016 at SMEAR II station (Hari and Kulmala, 2005) in a boreal forest located in southern Finland, together with meteorological parameters and other measured trace gas variables to investigate the variations in the concentrations and vertical profiles of ozone. We aimed to make a statistical evaluation of the low ozone concentration episodes and characterise the atmospheric conditions associated with the observation of these low concentration episodes to identify key atmospheric features during the ozone depletion events. A complete manuscript for this work is available on ACPD (Chen et al., 2017).

METHODS

Ozone and other trace gas as well as meteorological data were collected from the mast measurements at SMEAR II station (Hari and Kulmala, 2005). The measurements were performed at six different heights (4.2 m, 8.4 m and 16.8 m, 33.6 m, 50.4 m and 67.2 m) before February 2013. Later two more measurement heights (101 m and 125 m) were introduced. Analyses were carried out based on 10-min data. Four low-concentration thresholds (10, 5, 2 and 1 ppb) were used to characterise low ozone concentration episodes. A low ozone concentration episode was considered as an ozone depletion event if it lasted for more than 30 min. Episodes that failed to fulfil the duration constraint of an ozone depletion event were referred as ozone concentration drops.
CONCLUSIONS

Daily median ozone concentrations were in the range of 20-50 ppb, with high concentrations observed in spring and low concentrations in the winter months. High ozone concentrations were typically seen during daytime, likely related to the photochemical production of ozone. In the vertical profile, the highest ozone concentrations were found above the canopy level. In general, ozone concentrations tended to decrease with decreasing heights.

Over the 20-year observations, we could identify, at 4.2 m based on 10-min data, on average more than a thousand of cases in every hour, during which ozone concentrations were below 10 ppb, and several tens of cases with ozone concentrations below 2 ppb. For ozone depletion events that lasted for more than 30 min, the frequency of observations was high in autumn and winter, which showed a decreasing tendency with increasing heights. The springtime was observed with the least number of ozone depletion events. We could also find a few cases of long-lasting (>3 hours) ozone depletion events. A statistical summary on these long-lasting events is shown in Table 1. Low ozone concentrations episodes were seen typically associated with low temperatures, low wind speeds, high relative humidities and limited intensity of solar radiation. These conditions are likely to occur upon the formation of a shallow mixing layer. Under such conditions, the enrichment process from residual layer and photochemical production of ozone are prohibited, but ozone continues to be lost through deposition and chemical consumption in the confined mixing layer.

Table 1. The number of ozone depletion events that last for more than 3 hours seen at different heights.

<table>
<thead>
<tr>
<th>Height [m]</th>
<th>67.2</th>
<th>50.4</th>
<th>33.6</th>
<th>16.8</th>
<th>8.4</th>
<th>4.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 10 ppb</td>
<td>148</td>
<td>141</td>
<td>178</td>
<td>202</td>
<td>241</td>
<td>356</td>
</tr>
<tr>
<td>&lt; 5 ppb</td>
<td>26</td>
<td>28</td>
<td>29</td>
<td>35</td>
<td>43</td>
<td>63</td>
</tr>
<tr>
<td>&lt; 2 ppb</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>5</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>&lt; 1 ppb</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 1. a) A near surface depletion on 14/15-Sep-2009. b) a full-profile depletion on 23-Oct-2006.

We further categorised ozone depletion events into two major types, namely full-profile depletion and near-surface depletion. In full-profile depletion, low ozone concentrations can be observed extended to 67.2 m resulting in a negligible concentration difference between 67.2 m and 4.2 m whereas a clear
concentration gradient exists in the vertical profile in the case of near-surface depletion, as exemplified in Figure 1. A detailed analysis on case studies of the two depletion types can be found in Chen et al. (2017).

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REFERENCES


INFLUENCE OF ATMOSPHERIC CONDITIONS ON PURE BIOGENIC NUCLEATION IN THE CLOUD CHAMBER

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Keywords: NEW PARTICLE FORMATION, CLOUD EXPERIMENT, OZONOLYSIS

INTRODUCTION

Atmospheric aerosols affect both human health (Harrison and Yin, 2000) and Earth’s radiative energy balance, either directly or indirectly via their influence on clouds (IPCC, 2013). New particle formation (NPF) by gas-to-particle conversion forms initial molecular clusters around 1 nm diameter, which then grow by vapour condensation and may reach sizes above around 50 nm, where they can act as cloud condensation nuclei (Kulmala et al., 2013). NPF is estimated to contribute to a substantial fraction of global cloud condensation nuclei (Merikanto et al., 2009; Kerminen et al., 2012). Originally, it was thought that NPF can only occur in the presence of sulfuric acid vapour (Kuang et al., 2008) and that ions do not play a major role (Hirsikko et al., 2011, and references therein). However, chamber and laboratory experiments have shown that particles can form from organic precursors in the absence of sulfuric acid (Zhao et al., 2013; Kirkby et al., 2016). Our experiments are of atmospheric relevance as they simulate new particle formation in locations where sulfuric acid is rather scarce like the Amazonian forest (Wimmer et al., 2017) and the free troposphere (Bianchi et al., 2016). They also reflect the occurrence of pure biogenic nucleation in the pristine pre-industrial era where no anthropogenic pollutants were present (Gordon et al., 2016).

Kirkby et al. (2016) presented evidence for pure biogenic particle formation solely from highly oxidized α-pinene oxidation products under atmospheric conditions in the CERN CLOUD (Cosmics Leaving OUtdoor Droplets) chamber. Kirkby et al. (2016) also showed that ions from galactic cosmic rays enhance the particle formation rates by up to a factor 10-100 in the system investigated in their study. Ion-induced nucleation is therefore the main pathway for the formation of initial clusters from highly oxygenated molecules (HOMs) resulting from ozonolysis of biogenic vapours.
The discovery of pure biogenic nucleation reported by Kirkby et al. (2016) resulted from ozonolysis of a single monoterpene (α-pinene) at 5°C and in the absence of other vapours. Here we report pure biogenic nucleation rates measured in the CLOUD chamber in 2015 and 2016, and extend the original study to include for the first time several biogenic vapours - monoterpene, sesquiterpenes and isoprene - under a range of environmental conditions (NOx, ion concentrations, relative humidity, daytime/nighttime conditions and temperature). Our aim is to study the influence of a more realistic atmospheric conditions on pure biogenic nucleation.

METHODS

The CLOUD experiment at CERN (Kirkby et al., 2011; Duplissy et al., 2016; Kirkby et al., 2016) is designed to study particle formation under extremely low contamination levels and precisely controlled conditions. The 3-m-diameter stainless-steel chamber enables a detailed investigation of the effects of cosmic rays on aerosols, cloud droplets and ice particles under atmospheric conditions. The large volume (26.1 m³) and dual internal mixing fans result in homogeneous and highly stable operating settings. The CLOUD chamber has an advanced gas system that maintains stable precursor gas concentrations in the desired 1 pptv – 10 ppbv range. To maintain low contamination, the electro-polished chamber walls are periodically cleaned with ultra-pure water and then heated to 100°C during a cleaning cycle that lasts between 1 and 3 days. To further minimize contaminants, the chamber is supplied with synthetic air from evaporation of liquid nitrogen and liquid oxygen, mixed in the ratio 79:21. Ozone is introduced into the chamber, normally in the range of 10-40 ppbv, but as high as 1 ppmv when a cleaning cycle is in progress in order to help remove organic contaminants.

The accurate control of the chamber properties along with its high cleanliness allows particle formation to be studied under atmospherically relevant conditions. Moreover, the chamber can be exposed to a pion beam from the CERN Proton Synchrotron to allow the control of the ion-pair concentrations in the chamber between ground level and the lower stratosphere. Furthermore, the chamber is equipped with high voltage electrodes for creating an ion-free environment and measuring so-called “neutral” (uncharged) nucleation. By subtracting the neutral nucleation rate from the GCR or pion beam rates, the ion-induced nucleation rate can be determined.

The new measurements to be reported here were made during the CLOUD10 (September to December 2015) and CLOUD11 (September to November 2016) campaigns. The experiments started with different concentrations of pure monoterpene (α-pinene and δ-3-carene, individually and then as a mixture) at different temperatures (-25, 5, 25 °C). In later experiments, a sesquiterpene (β-caryophyllene) and isoprene were studied both individually and in a pure biogenic “soup” together with monoterpene (α-pinene). The nucleation rates resulting from the oxidation of the mixture under varying conditions were measured. Different atmospheric environments were simulated in the CLOUD chamber by varying the NOx concentration (and its photolysis rate), UV irradiation, ion concentration (neutral vs. ion-induced nucleation), relative humidity (0-80%) and temperature (-35 to 25 °C). An example of pure biogenic particle formation from a soup of α-pinene, isoprene and β- caryophyllene at 5 °C is shown in Figure 1. Upon increasing the concentrations of the individual components of the mixture, an increase in nucleation and growth rates is evident. The size distribution was measured with three instruments, a scanning PSM (Vanhanen et al. 2011), a DMA-train (Stolzenburg et al. 2016) and a TSI nano-SMPS (Wang and Flagan 1990). Figure 2 displays the difference in the oxidation products resulting from ozonolysis of different combination of biogenic volatile organic compounds. While the addition of isoprene to α-pinene results in a decrease of compounds with 20 carbons, the addition of β-caryophyllene results in the appearance of compounds with 30 carbons accompanied with an increase of formation rate of particles. The oxidation products are measured using a nitrate ion based chemical ionization atmospheric pressure interface time of flight mass spectrometer (CI-APiTOF; Jokinen et al., 2012). The exact mechanism by which this process takes place is still under investigation.
CONCLUSIONS

Biogenic vapours alone can form particles at rates comparable to sulfuric acid – ammonia/DMA systems under low-pollution conditions. During the CLOUD10 and CLOUD11 campaigns we carried out the first study of the effect of different atmospheric conditions on pure biogenic nucleation using an atmospherically-relevant mixture of monoterpenes, a sesquiterpene and isoprene. In particular, we studied the effect of NOx on the pure biogenic nucleation rates under night-time and daytime conditions, which modifies the properties of extremely low volatility organic compounds (ELVOCs) – the subset of HOMs that are mainly responsible for particle nucleation.

The well-controlled, low contamination CLOUD chamber at CERN has enabled us to perform a wide-range of experiments on pure biogenic nucleation under realistic atmospheric conditions. We are able present a first picture of pure biogenic nucleation under conditions corresponding to night-time boreal forests, NOx-polluted forested regions, tropical rain forests at low and high altitudes, and the pristine pre-industrial climate.

Figure 1. The time evolution of the number size distribution during a typical pure biogenic new particle formation experiment in the CERN CLOUD chamber. The size distribution is measured with three instruments: a scanning PSM (1.2-2 nm), a DMA-train (2-8 nm) and a TSI nano-SMPS (8-65 nm). The concentrations of the precursor gases (indicated above the picture) were increased in three steps, resulting in increasing nucleation and growth rates.

Figure 2. Concentration of highly oxidized molecules grouped according to their carbon number observed during different ozonolysis experiments and measured with CI-APi-TOF. All experiments were performed at 5 °C and under 40 ppb of ozone. AP is pure α-pinene, IP is pure isoprene, AP + IP is a mixture of α-pinene and isoprene, BCY is pure β-caryophellene and AP + IP + BCY is the mixture of α-pinene, isoprene and β-caryophellene. Concentrations of gases accompanying the plot are the measured concentrations during the experiment.
ACKNOWLEDGEMENTS

We thank the European Organization for Nuclear Research (CERN) for supporting CLOUD with important technical and financial resources and for providing a particle beam from the CERN Proton Synchrotron. This research has received financial support from each of Academy of Finland (Center of Excellence project no. 1118615), Academy of Finland (135054, 133872, 251427, 139656, 139995, 137749, 141217, 141451), Finnish Funding Agency for Technology and Innovation, Nessling Foundation, US Department of the EC Seventh Framework Programme (Marie Curie Initial Training Networks) ‘CLOUD-TRAIN’ (no. 316662), Energy, grant no DE-SC0014469, ERC-Consolidator Grant NANODYNAMITE 616075, Marie Sklodowska-Curie Grant 656994 ("Nano-CAVa"), the Presidium of the Russian Academy of Sciences, the Program "High energy physics and neutrino astrophysics" 2015, ERC-Starting grant COALA, grant no. 638703, ERC-Starting grant QAPPA, grant no. 335478, US Department of Energy, grant no DE-SC0014469, the German Federal Ministry of Education and Research (project nos. 01LK0902A and 01LK1222A), the Swiss National Science Foundation (project nos. 200020_135307 and 206620_130527), the Austrian Science Fund (FWF; project no. P19546 and L593), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/2010), the Swedish Research Council, Vetenskapsrådet (grant 2011-5120). Part of this work was supported by the Doctoral Programme in Atmospheric Sciences (ATM-DP, University of Helsinki).

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Keywords: cloud, probes, in-situ, sub-Arctic.

INTRODUCTION

Clouds are a major component of the atmosphere that plays a significant role in the climate system due to their ability to scatter and absorb radiation. Nowadays, clouds and their interaction with aerosol particles are poorly understood and provide some of the greatest uncertainties in predictions of climate change. The main cloud microphysical parameters in studying aerosol cloud interactions are the total number concentration, the effective radius of cloud droplets and the cloud liquid water content (Komppula et al., 2005; Lihavainen et al., 2008).

Semi-long term measurements of in-situ cloud droplet concentrations were carried out during Pallas Cloud Experiments (PaCE) at Pallas-Sodankylä Global Atmosphere Watch (GAW) station, in northern Finland in autumn of 2012, 2013 and 2015. Our main motivation during those campaigns was to investigate aerosol-cloud interactions using in-situ measurements techniques.

METHODS

FMI's Pallas-Sodankylä Global Atmosphere Watch (GAW) station is located in Finnish sub-Arctic region. It is part of the national park, with limited access. Sammaltunturi station (67°58’N, 24°07’E, 560 m a.s.l.) is the main measurement site. It is considered as a great place for ground-based observations of low level and orographic clouds. During autumn, Sammaltunturi measurement site is usually about 50% of time inside a cloud. In-situ cloud properties are measured by two different cloud probes installed on the roof of the station: a Forward Scattering Spectrometer Probe (FSSP, 3-47 µm, model SPP-100, DMT) and the Cloud, Aerosol and Precipitation Spectrometer (CAPS, DMT), which includes three instruments: the Cloud Imaging Probe (CIP, 12.5 µm-1.55 mm), the Cloud and Aerosol Spectrometer (CAS-DPOL, 0.51-50 µm) with depolarization feature, and the Hotwire Liquid Water Content Sensor (Hotwire LWC, 0 - 3 g/m³), see Fig 1B, C. In this abstract, examples of results from the analysis of the cloud properties measured by CAS and how they were influenced by meteorology are presented. All meteorological data were measured from Vaisala FD12P weather sensor (Hataka et al., 2003).

For the estimation of the presence of a cloud at the measurement site we used the cloud droplet counts measured with both the cloud probes. Also, the number concentration was crosschecked against the visibility measurements. Finally, we considered that the station was inside a cloud while we had droplet counts measured by the cloud probes, the horizontal visibility was less than 1000 meters and the relative humidity was around 100%.
Figure 1. A) FSSP-100 and B) CAPS probes as they were installed on Sammaltunturi measurement site during PaCe2015.

RESULTS

In this work, minute averages from each cloud probe were calculated when the station was inside a cloud. The raw CAS data were cleaned for the wind direction, because CAPS was installed at fixed direction (the main wind direction) and FSSP was installed on a rotating platform with the ability to follow the wind direction. When the wind direction is perpendicular to the fixed set direction, the CAS probe heavily undercounts compared to FSSP-100 (Doulgeris et al., 2016). Further correction for coincidence and dead time losses for the FSSP probe were not applied in those examples because number concentrations that were measured were lower than 300 #/ccm (Baumgardner et al., 1985).

PaCE 2012 took place from September 13th till October 30th; PaCE 2013 took place from September 14th till November 28th and PaCE 2015 took place from October 6th till December 2nd. As a cloud event we defined the situation when the station was inside a cloud for at least one continuous hour. In each year around 70% of the days of the campaign a cloud events were observed. CAPS and FSSP-100 data coverage were around 90% for each campaign and average wind speed when the station was inside a cloud was 6.5 (2.4), 7.3 (2.8) and 6.85 (2.4) m/s respectively for PaCE 2012, 2013 and 2015.

The averaged cloud properties for several campaigns are summarized in Table 1. It presents the averaged values along with standard deviations of the effective diameter ($ED_{CAS}$), the median volume diameter ($MVD_{CAS}$) and the liquid water content ($LWC_{CAS}$) as they were measured from CAS probe for the three campaigns.
<table>
<thead>
<tr>
<th>Campaign</th>
<th>$\text{ED}_{\text{CAS}}$ (um)</th>
<th>$\text{MVD}_{\text{CAS}}$ (um)</th>
<th>$\text{LWC}_{\text{CAS}}$ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PaCE 2012</td>
<td>14.10 (5.21)</td>
<td>15.39 (5.46)</td>
<td>0.040 (0.032)</td>
</tr>
<tr>
<td>PaCE 2013</td>
<td>13.38 (2.35)</td>
<td>14.86 (4.25)</td>
<td>0.025 (0.020)</td>
</tr>
<tr>
<td>PaCE 2015</td>
<td>12.28 (5.10)</td>
<td>13.38 (5.38)</td>
<td>0.029 (0.027)</td>
</tr>
</tbody>
</table>

Table 1. Averaged data of $\text{ED}_{\text{CAS}}$, $\text{MVD}_{\text{CAS}}$ and $\text{LWC}_{\text{CAS}}$ along with corresponding standard deviations (in brackets) when the station was inside a cloud for all three campaigns.

Figure 2 shows the number concentration ($N_c$) timelines, liquid water content ($LWC$) and median volume diameter ($MVD$) as they were measured with CAS probe for all the three PaCE campaigns along with the temperature trends at altitude of 570m while the station was inside a cloud. Number concentration averaged values are similar for every year of the measurements and reach scales around 100 #/ccm. However, there are cases that number concentration during a cloud event had values around 250 #/ccm. Each year the temperature trends and ranges were similar. In particular, in 2012 temperature range were from -9.5 to 6.6 °C, in 2013 from -12.0 to 9.9 °C and in 2015 from -7.0 to 4.7 °C.

Figure 2. Number concentrations, liquid water content and median volume diameters timelines for PaCE 2012, 2013 and 2015 are shown as they were measured by CAS probe when the measurement site was inside a cloud. The daily averaged data for the temperature versus time for each campaign is also presented.
ACKNOWLEDGEMENTS

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EFFECT OF ARCTIC SEA ICE ON AEROSOLS IN EASTERN LAPLAND

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Keywords: Aerosol concentration, aerosol size distribution, Arctic sea ice, Arctic Oscillation.

INTRODUCTION

Aerosol concentrations and size distributions observed in certain location depend on the sources and sinks in the air mass history. These are on the other hand much influenced by the underlying surface. In the Arctic, relevant surface types are land, open ocean and sea ice. Both the surface area and volume of Arctic sea ice is declining rapidly (Stroeve, 2007). Changes in sea ice are expected to affect the aerosol concentrations at stations in the continental Arctic, if air masses travel over areas once covered in sea ice. However, changes in sea ice have also been noted to either cause changes to large-scale atmospheric circulation patterns or to be caused by changes to the large-scale circulation. Thus, potentially changes in sea-ice extent or concentration can indirectly influence aerosol concentrations: the altered sea-ice extent acts to alter the circulation and thus air masses which arrive and are observed in eastern Lapland, will have different source regions and will have travelled over different land surfaces. Here we show, how aerosol concentrations and size distributions observed at SMEAR I station in eastern Lapland, Finland, depend on the time that trajectories spend over sea ice, open ocean or land. We also show how aerosol concentrations at SMEAR I are correlated with large-scale circulation indices NAO (North Atlantic Oscillation) and AO (Arctic Oscillation). Finally, we show how the total sea ice extent and sea ice extent in specific areas influence the aerosol concentrations observed at SMEAR I.

METHODS

In our analysis we used aerosol size distribution data measured with the DMPS (Differential Mobility Particle Sizer), trace gas concentration data, Arctic sea ice concentration data from NSIDC (National Snow and Ice Data Center), daily North Atlantic Oscillation (NAO) and Arctic Oscillation (AO) indices and HYSPLIT back trajectories. First, we calculated median aerosol size spectrums and concentrations for days with at least 15 DMPS spectra. Then, we binned those according to how many hours the air mass had spent over consolidated pack ice (sea ice concentration, SIC > 80%), open pack ice (SIC > 15%), open sea and land. For this, only data with more than 10 days in each bin was considered. Also, only trajectories which had spent >90% of their travel time north of SMEAR I were taken into account. Furthermore, we tested the sensitivity of the results by removing all trajectories with time over land (TOL) more than 40 hours and excluding all data with SO₂ above 75th percentile. If trajectories spend more than 40 hours over land the effect of the land surface dominated and the impact of sea ice or open sea was not evident. By removing high SO₂ peaks we could neglect the effect of high sulfur to aerosol concentrations (Kyrö, 2014). We calculated linear regressions to the modal and total aerosol number concentrations and mode peak diameters as a function of trajectory’s travel time over sea ice (TOSI80, TOSI15), time over open sea (TOOS), and TOL. We also looked at the sea ice area (SIA) in different sea areas, namely Arctic Ocean (AOC), Greenland Sea (GRS) and Kara and Barent’s Seas (KBS), and compared it to the aerosol concentrations during negative or positive phase of NAO and AO. Since the aerosol concentration is strongly dependent on temperature (Paasonen, 2013), we only looked at temperature range -10-0°C. Within this range, the median accumulation mode concentration is not dependent on temperature at SMEAR I.
During summer, the total aerosol number, Aitken mode and accumulation mode concentrations were decreasing with increasing time the air mass spent over the sea ice by -8.9, -5.3 and -1.6 cm$^3$/h, respectively (Table 1). The Aitken mode diameter was decreasing -0.3 nm/h and the accumulation mode diameter -0.5 nm/h (Table 2). During winter there was a decrease in total, nucleation mode and Aitken mode concentrations (-1.3, -0.3, -0.6 cm$^3$/h, respectively). During winter these trends were remarkably smaller. The only statistically significant relationship for modal concentrations and TOOS was for accumulation mode: -0.4 cm$^3$/h. Since the number concentration of potential CCN decrease with increasing time over sea ice in summer, this can affect the cloud properties and radiation balance in the Arctic in the future as the sea ice area continues to decrease. During the winter on the other hand, the concentration of potential CCN increase with increasing time over open sea and can again affect the aerosol-cloud-climate interactions.

Aerosol concentrations were generally increasing with increasing SIA. Statistically most significant relationship was found between accumulation mode concentration and SIA, especially in Kara and Barent’s Seas. This is logical, since that area is closest to SMEAR I (Table 3). The relationship was stronger during positive NAO and AO and smaller during negative large-scale circulation indices. The decreasing sea ice is likely to favor the negative phase of both indices (Vihma, 2014). If only northerly air masses were taken into account, there was no difference in the strength of the relationship between NAO and AO positive or negative phases. It needs to be pointed out that SIA and TOSI, are not strongly correlated with each other and represent different air masses – majority of SIA values are observed with low TOSI values and represent all air masses whereas there is a large variation of TOSI for high SIA values and TOSI is calculated only for air masses that have been north of SMEAR I.

Table 1 Trends in aerosol number concentrations as a function of TOSI80, TOSI15, TOOS and TOL, during summer and winter. Statistically significant p-values are bolded. Those trends were both p≤0.05 and R$^2$≥0.5 are shaded with grey. Trends where p≥0.05 and R$^2$≤0.15 are not shown. High SO$_2$ peaks and TOL>40h have been removed from the data.

<table>
<thead>
<tr>
<th></th>
<th>Summer [cm$^3$/h]</th>
<th>R$^2$</th>
<th>p</th>
<th>Winter [cm$^3$/h]</th>
<th>R$^2$</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TOSI80</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total concentration</td>
<td>-8,9</td>
<td>0,56</td>
<td>0,016</td>
<td>-1,3</td>
<td>0,56</td>
<td>0,004</td>
</tr>
<tr>
<td>Nucleation mode</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aitken mode</td>
<td>-5,3</td>
<td>0,64</td>
<td>0,016</td>
<td>-0,6</td>
<td>0,69</td>
<td>0,002</td>
</tr>
<tr>
<td>Accumulation mode</td>
<td>-1,6</td>
<td>0,98</td>
<td>0,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TOSI15</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total concentration</td>
<td>-6,6</td>
<td>0,76</td>
<td>0,009</td>
<td>-0,9</td>
<td>0,33</td>
<td>0,033</td>
</tr>
<tr>
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<td>0,56</td>
<td>0,029</td>
<td>-0,3</td>
<td>0,26</td>
<td>0,012</td>
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<tr>
<td>Aitken mode</td>
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<td>0,81</td>
<td>0,009</td>
<td>-0,6</td>
<td>0,71</td>
<td>0,001</td>
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<td>0,96</td>
<td>0,001</td>
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<tr>
<td><strong>TOOS</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total concentration</td>
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<td>0,16</td>
<td>0,193</td>
<td></td>
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<tr>
<td>Nucleation mode</td>
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<td>Aitken mode</td>
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<td>0,034</td>
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<tr>
<td>Accumulation mode</td>
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<td>0,43</td>
<td>0,150</td>
<td>-0,4</td>
<td>0,38</td>
<td>0,189</td>
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<tr>
<td><strong>TOL</strong></td>
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<td></td>
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<tr>
<td>Total concentration</td>
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<td>0,63</td>
<td>0,020</td>
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<td></td>
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<tr>
<td>Nucleation mode</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Aitken mode</td>
<td>6,3</td>
<td>0,74</td>
<td>0,002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accumulation mode</td>
<td>2,8</td>
<td>0,66</td>
<td>0,001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2: Trends in Aitken and accumulation mode peak diameter as a function of TOSI80, TOSI15, TOOS and TOL, during summer and winter. Statistically significant p-values are bolded. Those trends were both \( p \leq 0.05 \) and \( R^2 \geq 0.5 \) are shaded with grey. Trends where \( p \geq 0.05 \) and \( R^2 \leq 0.15 \) are not shown. High SO\(_2\) peaks and TOL>40h have been removed from the data.

<table>
<thead>
<tr>
<th></th>
<th>Summer [nm/h]</th>
<th>( R^2 )</th>
<th>( p )</th>
<th>Winter [nm/h]</th>
<th>( R^2 )</th>
<th>( p )</th>
</tr>
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<tbody>
<tr>
<td>TOSI80</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Aitken</td>
<td>-0.3</td>
<td>0.62</td>
<td>0.029</td>
<td>-0.5</td>
<td>0.98</td>
<td>0.024</td>
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<tr>
<td>Accumulation mode</td>
<td></td>
<td></td>
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<tr>
<td>TOSI15</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Aitken</td>
<td>-0.4</td>
<td>0.91</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
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<td></td>
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<tr>
<td>TOOS</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aitken</td>
<td>0.3</td>
<td>0.71</td>
<td>0.007</td>
<td></td>
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<tr>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Aitken</td>
<td>0.4</td>
<td>0.48</td>
<td>0.013</td>
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<tr>
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<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Table 3: Trends in nucleation, Aitken and accumulation mode as a function of SIA in the Arctic and in different sea areas in the Arctic in winter (temperature range -10-0°C). Statistically significant p-values are bolded. Those trends were both \( p \leq 0.05 \) and \( R^2 \geq 0.5 \) are shaded with grey. Trends where \( p \geq 0.05 \) and \( R^2 \leq 0.2 \) are not shown.

<table>
<thead>
<tr>
<th></th>
<th>Nucleation mode [#/10^6km^2]</th>
<th>( R^2 )</th>
<th>( p )</th>
<th>Aitken mode [#/10^6km^2]</th>
<th>( R^2 )</th>
<th>( p )</th>
<th>Accumulation mode [#/10^6km^2]</th>
<th>( R^2 )</th>
<th>( p )</th>
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<td></td>
</tr>
<tr>
<td>All</td>
<td>1.3</td>
<td>0.59</td>
<td>0.22</td>
<td>2.4</td>
<td>0.86</td>
<td>0.03</td>
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<td></td>
</tr>
<tr>
<td>NAO &lt; -0.5</td>
<td>-0.2</td>
<td>0.31</td>
<td>0.81</td>
<td>0.9</td>
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</table>
CONCLUSIONS

Arctic sea ice has strong impact on the aerosol concentrations measured at SMEAR I in eastern Lapland, Finland and the changes in the sea ice extent and time that the air parcel spends over sea ice can have an influence on the aerosol-cloud interactions in the continental Arctic. The concentrations of potential CCN have contrasting trends with decreasing sea ice during summer and winter. However, low-level clouds over white surfaces (wintertime Arctic) have a net warming effect on climate. Thus, the net effect of decreasing sea ice to climate through aerosol-cloud interactions might be cooling both during summer and winter.

ACKNOWLEDGEMENTS

This work was supported by the Nordic Centre of Excellence CRAICC (Cryosphere-atmosphere interactions in a changing Arctic climate), Academy of Finland Centre of Excellence program (project no. 307331) and the European Research Council (project no. 227463).

REFERENCES


INSIDE A VOLCANOE PLUM: NEW PARTICLE FORMATION MEASURED WITH A FLYING MASS SPECTROMETER

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Keywords: Sulfuric acid, new particle formation, STRAP, CLERVOLC, API-TOF, Volcano’s plume, Flight measurement.

INTRODUCTION

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

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

METHODS

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

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

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

ACKNOWLEDGEMENTS

This work was supported by Labex ClerVolc (programme 1), ANR STRAP projects, and by the Academy of Finland Center of Excellence programme (grant no. 307331).

REFERENCES

INTERCOMPARISON OF SIX PARTICLE COUNTERS – IMPACT ON EDDY COVARIANCE MEASUREMENT DATA

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Keywords: PARTICLE COUNTER, EDDY COVARIANCE, AEROSOL.

INTRODUCTION

Eddy covariance measurement of aerosol fluxes combine fast (10 Hz) particle concentration measurements, and 3-D wind data to determine the vertical exchange of aerosol particles. These measurements are performed at numerous sites around the world, however, the instrumentation at these sites is far from homogenous, with multiple different wind probes, measurement platforms and particle counters being used. The fast sampling rate is required in order to capture more of the vertical exchange, as eddies transporting the particles are fast and short lived. However, all of the commonly used CPC’s have response time considerably longer than the 0.1 s required by the eddy covariance method, which in part contributes to the large uncertainties associated with particle flux measurements (Pryor et al., 2008). Here we studied the effect of different particle counters on the particle flux measurements, by having six particle counters with differing properties sampling from the same line over a boreal forest in Hyytiälä, Finland.

METHODS

The eddy covariance measurements were performed in Hyytiälä, Finland, on a tower based platform at the height of 35 m. The measurement period was from 24th of April to the 22nd of May, 2017. The set ups consisted of a METEK USA-1 type sonic anemometer and the six different condensation particle counters (CPC) listed in Table 1. All particle counters were recorded at 10 Hz and differed in their response time, sample flow and cut-off size, which were expected to influence the results.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Model</th>
<th>Nominal cut-off (nm)</th>
<th>Response time (s)*</th>
<th>Sample flow (cm³ s⁻¹)</th>
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<td>16.7</td>
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<td>Brechtel</td>
<td>MCPC</td>
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<td>~ 0.2</td>
<td>6.0</td>
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</table>

Table 1. List of instrumentation used in the intercomparison campaign, along with their cut-off sizes and reported response times.*Response time is determined as the time taken for a concentration change of 95 %, not including dead time before initial change

In order to minimize the influence of the tower on the wind profile the wind probe and aerosol inlet were placed at the end of a 4 m long boom off the platform edge. The sampling line had a total length of 4.5 meters for the first instrument in the line, and an inner flow of 20.1 lpm. The length between the first and the last CPC in the line was < 1 m. The flow was held turbulent all the way to the last instrument in the line, by providing 12 lpm of excess vacuum in the 4 mm inner diameter sampling line.
CONCLUSIONS

The time series of all CPC’s showed good agreement between the different particle counters (Fig. 1). During presumed nucleation events, the impact of the different lower detection limits between different CPC’s was observed, with the more sensitive particle counters showing larger concentrations. This behaviour was observed also in the diurnal cycle. Disagreement between the particle counters became larger in the hours around noon, where newly formed particle typically grow up to 4 – 10 nm in diameter, which is around the detection limit of these CPCs (e.g. Kulmala et al., 2004).

Figure 1. Time series of particle concentration over the measurement campaign showing good agreement between the different CPCs. Lower detection limit dependent events can be seen associated with the two highest concentration peaks.

As expected, the instruments with a smaller sample flow were found to have a larger statistical uncertainty associated with them (Fig. 2). This is to be expected, as the measured concentration is effectively calculated from a smaller subset of measured particles and the amount of counts is directly related to the amount of uncertainty in the data (Kangasluoma and Kontkanen, 2017). For the range of instruments present here, the uncertainty in the particle concentration ranged from 2 – 9 %.

Figure 2. Mean statistical uncertainty of the recorded concentration and observed variance as a function of sampled aerosol flow.

The instruments with faster response times showed higher variance, which is partially explained by them more accurately capturing the rapid fluctuation in particle concentrations and partially by the lower sampling flows used. This means that the improvements in data quality provided by the faster response time are partially masked to by the added random noise in the measurements. The opposite case can be observed with the slowest instruments, such as the TSI 3010. It shows very low statistical uncertainty, but is unable to distinguish the fastest eddies, and in effect buffers them out resulting in an unrealistically low variance. Therefore, neither of the extremes provide ideal data for flux measurements.
As the eddy covariance method has numerous sources for uncertainty, it would be ideal not to increase these with a poor choice for a CPC (Rannik et al., 2016). This means choosing CPCs with sufficiently high sample flows, if 10 Hz sampling is practiced. As the relationship between uncertainty and sample flow is not linear, flows smaller than 0.3 lpm should be avoided in most environments. For low concentration environments like the boreal forests, the sample flows should preferably be still higher, ideally more than 0.5 lpm.

ACKNOWLEDGEMENTS

This work was supported by the Academy of Finland Center of Excellence programme (grant no. 307331) and by the Maj and Tor Nessling Foundation, grant 201700367. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 654109. We would like to acknowledge Brechtel Mfg. Inc for providing instrumentation for the campaign.

REFERENCES


During daytime, plants take up carbon dioxide (CO\textsubscript{2}) through the process of photosynthesis but at the same time they also respire CO\textsubscript{2}. During nighttime, in the lack of solar radiation, CO\textsubscript{2} exchange (flux) is solely composed of respiration of plants and forested ecosystems act as sources of CO\textsubscript{2}. The photosynthetic sink of CO\textsubscript{2}, described by gross primary production (GPP), is traditionally defined from direct eddy covariance (EC) measurements of CO\textsubscript{2} flux (NEE) taking into account respiration (R) defined from the night-time data as

\[
GPP_{eco} = R - NEE
\]

The problem with this method is the accurate determination of ecosystem respiration especially during daytime, and more direct methods are needed. The scientific community investigating carbon cycles has recently introduced a novel method for estimating terrestrial photosynthetic sink using carbonyl sulfide (COS), since plants take up COS in a similar way as CO\textsubscript{2} via stomata (Wohlfahrt \textit{et al.}, 2012; Berry \textit{et al.}, 2013). In contrast to CO\textsubscript{2}, there is no back-flux (respiration) of COS by plants and GPP can be calculated using equation

\[
GPP_{COS} = -\frac{F_{\text{COS}}}{LRU} [CO_2]_{COS}
\]

where \(F_{\text{COS}}\) is the COS flux, LRU leaf-scale normalized ratio of COS to CO\textsubscript{2} assimilation rate and [CO\textsubscript{2}] and [COS] concentrations of CO\textsubscript{2} and COS, respectively (Sandoval-Soto \textit{et al.}, 2005; Asaf \textit{et al.}, 2013). However,
studies have found nocturnal uptake of COS at the ecosystem level (Billesbach et al., 2014, Kooijmans et al., 2017) although photosynthesis has stopped due to lack of solar radiation. Explanations have included both soil uptake and incomplete closure of stomata during nighttime (Maseyk et al., 2014; Commane et al., 2015). Thus, it is important to measure both contributions simultaneously.

METHODS

The study site Hyytiälä scots pine forest is situated in Southern Finland (61°85’N, 24°29’E). Measurements were done in the SMEAR II station in the middle of a managed forest during the growing season 2016. Eddy covariance (EC) flux measurements of COS started already in 2013 at 23 m height above the canopy. The system consists of a Gill HS-1199 sonic anemometer (Gill Instruments, UK) for wind measurements, a continuous wave - quantum cascade laser spectrometer (QCLS, Aerodyne Research, USA) for measuring COS, CO₂, H₂O and CO mixing ratios (Kooijmans et al., 2016) and LI-6262 (LI-COR Inc., USA) analyzer for CO₂ and H₂O mixing ratios at 10 Hz measurement frequency. Measurement campaign in 2016 included another QCLS (Aerodyne Research, USA) for measuring fluxes from three automatic soil chambers (LI-8100 soil chambers, LI-COR, USA) over different vegetation types, three branch chambers (pine and aspen) and concentration profile above and within the canopy.

RESULTS

Preliminary results show night-time ecosystem uptake of COS (negative flux) that is about 15% of the daily uptake. Soil chambers show constantly negative COS fluxes, although there is no uptake of CO₂ and the soil flux is about 25% of the total ecosystem flux. Pine and aspen branches seem to be sinks of COS throughout the day indicating open stomata during night-time. These findings suggest that negative ecosystem COS flux can be explained by both soil and vegetation uptake during night-time. From branch chamber measurements we were able to calculate the leaf relative uptake (LRU) separately for aspen and pine. We find that LRU has an exponential correlation with photosynthetic active radiation (PAR) when PAR<500 mol m⁻² s⁻¹. On the other hand, when PAR>500 mol m⁻² s⁻¹, the LRU seems to be constant and for aspen LRU=1.7 and for pine LRU=1.4. We find that the light dependency of LRU needs to be taken into account when calculating GPP from COS measurements for better photosynthesis estimates, as a constant LRU results in higher GPP especially during early morning and evening times (Fig. 1).
Figure 1. Diurnal cycles of GPP\textsubscript{COS} and GPP\textsubscript{eco} measured with EC technique, when using constant LRU=1.4 (left) and a radiation-dependent LRU (right) in Eq. 2.

CONCLUSIONS

Carbonyl sulfide fluxes over a boreal forest were measured with soil and branch chambers while ecosystem scale flux was monitored via eddy covariance measurements. Negative ecosystem scale COS flux is explained by both soil uptake and incomplete stomatal closure during night-time. We found that using a radiation-dependent LRU ratio leads to better GPP estimates than a constant LRU.

ACKNOWLEDGEMENTS

Special thanks to Helmi Keskinen, Heikki Laakso, Janne Levula and other Hyytiälä Forestry field station staff for all their technical support and help during the campaign. This study was supported by the Finnish Center of Excellence (272041) and ICOS-Finland (281255). The measurement campaign is part of a project that has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 654182.

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CONDENSATION SINK IN THE ATMOSPHERE:
A SIMPLE THEORETICAL MODEL FOR INTERMEDIATE KNUDSEN NUMBERS

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Keywords: CONDENSATION SINK, FUCHS-SUTUGIN COEFFICIENT.

INTRODUCTION

Condensation sink (CS) is an important parameter for aerosol dynamics quantifying the rate of the vapour condensation on the existing aerosol population. A time scale \( \tau = 1/\text{CS} \) has a clear physical meaning of a characteristic time for vapours to be condensed onto the surface of existing aerosol. Due to the similarity between the processes of vapour condensation on aerosol particles and coagulation of the smallest particles (monomers, dimers, clusters) with the larger particles from Aitken and accommodation modes, CS proves useful for the quantification of a coagulation sink (Lehtinen et al., 2007). Then a competition between the process of small clusters coagulation with the larger aerosol particles, represented by CS, and the process of the clusters growth by condensation, represented by the particle growth rate, defines the probability of clusters survival and a new particle formation event (Kulmala et al., 2017).

A simple model allowing to describe the dynamics of a condensation sink in the atmosphere thus could be helpful for understanding of new particle burst and cut-off processes. Our aim is to develop a model for the coupled dynamics of condensing vapours and aerosol using mainly analytical formulas. This approach allows to investigate in a simple way the contribution of different modes to the CS and discuss possible applications of CS for the quantification of climatic feedback loops including aerosol and solar radiation interaction.

METHODS AND RESULTS

Transformation of the mass flux towards the particle from the kinetic regime to the continuum regime is often described by the Fuchs-Sutugin coefficient (Fuchs and Sutugin, 1971). Kinetic regime can be obtained as a limiting case when only one term of the expansion of the Fuchs-Sutugin coefficient at large Knudsen numbers \( Kn \) is considered. Here we take into account the two first terms, and get the mass flux which agrees well with the full mass flux up to \( Kn \approx 0.5 \). This procedure allows to obtain an analytical solution of the condensation equation valid for the range of intermediate Knudsen numbers. We compare solutions in the kinetic regime and for intermediate Knudsen numbers. It is well-known that in the kinetic regime the number particle distribution does not change its shape, just the characteristic diameter grows in time (Seinfeld and Pandis, 2016). For intermediate Knudsen numbers the particle growth rate becomes diameter dependent and larger particles grow slower than smaller particles. This leads to narrowing of the number particle distribution.

The expansion is further applied to calculate analytically the condensation sink for the initial lognormal number particle distribution. We first discuss the difference between the CS calculated using a kinetic regime formula and the CS calculated using our approach. We show the parameter map that makes it possible to estimate the particle distribution parameters for which this difference becomes significant, i.e. define the limits of applicability of the kinetic regime formula for the CS calculations.
The formula is tested against experimental data measured in boreal forests and megacities. Our approach results in up to a 5.5% overestimate of the CS below 500 nm as compared to the calculations using the full Fuchs-Sutugin coefficient. The nucleation mode with a small characteristic diameter 2-3 nm does not contribute significantly to the atmospheric CS even for very high number concentrations (up to 10000 \(1/cm^3\)), while the accumulation mode with a characteristic diameter 100 nm and larger contributes even if the number concentrations are as low as 100 \(1/cm^3\).

By adding an equation for a vapour concentration to the formulas for CS, we develop a simple coupled model for the dynamics of the condensation sink and condensing vapours. The model in its present form can be used for the characteristic mode diameters larger than 20 nm. As many modes as needed can be included into the model. The only external parameter is the initial growth rate of the mode. The model describes adequately dynamics of the condensation sink in the atmosphere during the periods of the aerosol modes growth by condensation.

CONCLUSIONS

We have obtained a solution for the condensation equation in the range of intermediate Knudsen numbers (for particle diameters up to \(~500\) nm). The solution is based on taking two terms of the expansion for the Fuchs-Sutugin coefficient in terms of \(1/Kn\) at large \(Kn\) and is valid both for constant vapour pressure and (with small modifications) for vapour pressure changing in time.

We confirm the previous results by Lehtinen et al., 2003, that CS is defined mostly by larger particles and quantify the contribution of different modes to the CS, depending on the characteristic diameter of the mode and particle number concentration.

Note that the difference between CS in the kinetic regime and CS in the intermediate regime can be estimated using our formula. CS in the kinetic regime is proportional to the total surface of aerosol per unit volume. This same quantity appears in the extinction coefficient quantifying aerosol optical depth, an important parameter characterizing scattering and absorption of light by aerosol. Thus, one can deduce for what parameters CS is suitable to represent aerosol impact on the solar irradiance. For a typical lognormal distribution CS is proportional to the extinction coefficient if an aerosol mode is characterized by a particle number distribution with a mean geometric diameter less than \(~120\) nm. This is important to have in mind when choosing parameters for the quantification of biosphere-atmosphere feedback loops including aerosol and solar radiation interaction.

ACKNOWLEDGEMENTS

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THE EFFECT OF CHAMBER CONDITIONS ON PRODUCT DISTRIBUTION AND YIELD OF HIGHLY OXYGENATED MOLECULES IN BENZENE OXIDATION.

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INTRODUCTION

Secondary organic aerosol (SOA) is a significant constituent of particulate matter that forms through condensation of low volatile gaseous precursors (Hallquist et al. 2009). Oxidation of both biogenic and anthropogenic volatile organic compounds can lead to the low-volatility products that can contribute to SOA (Kroll and Seinfeld 2008). Several studies have tried to clarify the exact chemical composition of the condensing vapours; however, until recently, the available methods were insufficient for measurement of all condensing vapours (Hallquist et al. 2009). Developments in chemical ionisation mass spectrometry made it possible to identify a group of molecules called Highly Oxygenated Molecules (HOMs) as a significant contributor to growth of nanoparticles due to low- or extremely low- volatility (Ehn et al. 2014).

HOMs form in oxidation of biogenic volatile organic compounds (VOC), such as monoterpenes, sesquiterpenes and isoprene upon reactions with OH and ozone (Jokinen et al. 2014, Berndt et al. 2016, Jokinen et al. 2016). It was shown that these HOMs could be a missing link for explaining the rapid growth of small aerosol particles in the boreal forest and in laboratory experiments (Ehn et al. 2014, Tröstl et al. 2016). HOMs have also potential to aid new-particle formation through irreversible condensation on molecular clusters or by direct nucleation (Kulmala et al. 2014, Bianchi et al. 2016, Kirkby et al. 2016). While the research of HOMs from biogenic precursors is extensive, there is a lack of understanding of the role of HOMs in anthropogenic systems and consequently, urban areas.

Based on the previous research, aromatic compounds are the most prominent precursors for SOA among anthropogenic emissions (Kroll and Seinfeld 2008), which recently were shown to produce HOMs upon oxidation by OH (Garmash et al. in preparation, Molteni et al. 2016). In this study, we investigate the formation of HOMs from benzene oxidation at different chamber conditions with and without NOx. We study the yield of HOMs as well as the product distribution as a function of oxidant and VOC concentration. In addition, we perform comparison of chamber and flow reactor experimental systems. The understanding of how HOM composition change based on different environmental conditions will help to interpret the measurements in the urban atmosphere, provide direct evidence for results on aromatic SOA reported in the literature and discover new chemical pathways for aromatic oxidation.
METHODS

The chamber experiments were conducted at Jülich Atmosphere Plant Chamber (JPAC) at Forschungszentrum Jülich, Germany. We have tested a number of different conditions by varying the concentration of benzene as well as hydroxyl radical through regulation of ozone and light intensity. We have also added NO\textsubscript{2} and NO in order to identify the branching of HOMs due to oxidation termination reactions with NO\textsubscript{x}. HOMs were detected using nitrate-based chemical ionisation mass spectrometer (CI-APi-TOF), while VOC concentration was determined by proton-transfer reaction mass spectrometer (PTR-MS, I onicon).

The yield of HOMs was calculated using all identified HOM compounds with oxygen content of more or equal to 6, which represents the lowest estimate due to the assumption of collision-limited detection efficiency. In addition to benzene experiments, phenol oxidation was studied in order to elucidate the effect of secondary oxidation on the yield of HOM. Benzene, toluene and naphthalene oxidation was also tested in the flow reactor at the University of Helsinki.

RESULTS AND CONCLUSION

It was possible to estimate the HOM yield from oxidation of benzene and phenol in the JPAC chamber experiments. Figure 1 shows that the HOM molar yield increased significantly as the OH concentration in the chamber was increased. This positive relationship points at the second- or higher generation HOM products that were produced upon multiple OH attacks per one initial molecule of benzene. While only a few conditions were sampled for phenol as well as for benzene + NO\textsubscript{x} experiments, similar pattern is visible. In aromatic systems, generally, the oxidation products are much more reactive with OH than parent VOC, promoting a fast multi-generation oxidation.

![Figure 1. HOM molar yield in benzene oxidation (circles), phenol oxidation (diamonds) and oxidation of benzene in presence of NO\textsubscript{x} (crosses) at the JPAC chamber. Same masses from the spectrum were counted towards the HOM yield in all the experiments. The error on the yield determination arises from the error of HOM measurements, which is estimated as 50% (Ehn et al. 2014).](image-url)
From Figure 1, we can also see that phenol oxidation produced HOMs at somewhat lower yield than benzene oxidation, suggesting that part of the HOM are produced from non-phenolic pathway. The spectra produced by phenol (C₆H₅O) oxidation in JPAC chamber was surprisingly similar to the benzene (C₆H₆) experiments as long reaction time likely allows for a number of radical reactions bringing the product distribution closer to each other.

In benzene oxidation experiments, we observed a formation of highly oxidised N-containing HOMs in presence of both NO and NO₂ as well as upon only NO₂ addition. With CI-API-TOF, it was also possible to detect lower oxidized species, such as nitrophenol and nitrocathecol, which dominated the spectrum.

In comparison to the JPAC, flow reactor experiments with benzene produced fewer HOM with more distinct pattern suggesting steps of autoxidation (i.e. subsequent addition of O₂). As flow reactor experiment was performed at ppm level of benzene, the VOC-to-OH ratio is suggested as important variable affecting the distribution of HOM products.

We have observed that in aromatic systems both HOM yield as well as HOM composition will depend on the experimental parameters as well as on the presence of NOₓ. As HOMs are crucial in initial steps of SOA formation, these findings are important in interpreting the previous studies on SOA yields from oxidation of aromatics. Future studies will focus on systematic investigations of HOM and SOA composition in oxidation of benzene and toluene in the Helsinki chamber and flow-reactor.

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INTRODUCTION

Both atmospheric ice and dust are considered to play important roles in our climate system through their impacts on the radiative energy budget. On average, the Earth is nearly in a radiation balance: the amount of incoming solar radiation absorbed by the atmosphere and surface is balanced by nearly equal amount of longwave radiation emitted back to space. Even small changes in this planetary radiation balance can cause changes in the climate. In order to describe the interactions of the atmosphere with radiation, it is essential that its composition, including aerosols and cloud particles, is known. These interactions depend both on the properties of the radiation (wavelength and polarization) and particles (size, shape, and composition).

NONSpherical ATMOSPHERIC PARTICLES

In the atmosphere there are numerous particles originating from for instance, industrial and biological processes, deserts, volcanoes, and phase transitions of water vapour. Despite their sub-centimetre size, the particles influence conditions even globally. Of all atmospheric particles, we concentrate on these common particle types that have nonspherical shapes: ice crystals, mineral dust and volcanic ash. If these particles were assumed to be spherical, their radiative effects would be erroneously estimated. However, this simplification is widely used since the lack of exact, analytical solutions makes it very challenging to account for the nonspherical shapes realistically. In this poster, we summarize our latest results and ongoing research in finding and developing sufficiently accurate shape models as well as methods for solving the optical properties and radiative effects of ice crystals, mineral dust and volcanic ash. Our research on the single-particle optical properties is concentrated on the following topics:

- **Ice crystal** surface roughness and other non-idealities affects the optical properties of cirrus clouds (Haapanala, 2017) and the very existence of halo phenomena. We are developing a phenomenological, realistic model for rough surfaces over ice crystals and a computational methodology for considering wavelength-scale surface scatterers on an ice crystal much larger than the wavelength of light. We have also updated the ray optics code SIRIS by Muinonen et al. (2009) to correctly consider ray optics at the wavelengths where ice absorbs radiation – essentially throughout the near-infrared spectral region (Lindqvist et al., 2017).

- **Mineral dust** particles vary in sizes and shapes but they can also have different mineralogical compositions (Nousiainen, 2009). Merikallio et al. (2011) used light-scattering measurements of different mineral dust samples to establish a spheroid-based shape distribution that most accurately models light scattering by mineral dust. Haapanala et al. (2017) used these shape distribution to produce look-up-tables of optical properties of dust to be used in aerosol-climate model (Räisänen et al. 2013). On the other hand, Lindqvist et al. (2014) studied particle-to-particle variations in mineral dust optical properties in their pioneering approach where they made 3-dimensional models of dust particles using electron-microscope images of real dust particles,
computed their optical properties, and found large differences between different dust particle types.

- **Volcanic ash and dust** particles have typically porous structures (Fig. 1), which can have a major impact on the optical properties of these particles (Lindqvist et al., 2011), cause inaccuracies in retrievals of particle aspect ratios (Nousiainen et al., 2011), and lead to erroneous estimates of ash mass loadings from volcanic eruptions if modeled using spherical particles (Kylling et al., 2014).

![Figure 1. Examples of the various shapes of atmospheric a) ice crystals, b) mineral dust particle, and c) volcanic ash. We wish to thank Olga Munoz and Konrad Kandler for kindly providing us the images of the particles.](image)

**RADIATIVE TRANSFER MODELLING**

The non-spherical shape of atmospheric ice and dust particles yields uncertainties in our understanding how they interact with solar radiation. One of our aims is to better understand the impacts of particle size-shape distributions on optical properties and to radiative effects of ice and dust. The wavelength-dependent optical properties of these particles are essential to know for many applications. For example, they are needed for interpreting the remote sensing measurements from radars, lidars and satellite instruments. Depending on the application, ice crystals and dust particles can be either targets whose properties are to be measured, or objects interfering with the measurement of another target.

We use a unique way of connecting microphysical measurements of ice clouds via single-scattering properties to simulate radiation. In Haapanala (2017), the solar radiative effects of variously sized and shaped ice and mineral dust particles are simulated using radiative transfer models. In addition, a global aerosol–climate model is used to investigate the impact of dust particle nonsphericity on radiative effects of dust. This work takes advance of in-situ measured size-shape distribution of ice crystals and carefully validated shape models of dust particles (Merikallio et al., 2011). Haapanala (2017) offers interesting new insight into the connections between particle morphology, cloud microphysics and cloud radiative effects.

Our results show that in the shortwave radiative transfer perspective, the size, shape and concentration and roughness of ice crystals is important (Haapanala, 2017). Further, comparison of simulations to ground based radiation measurements suggest that most ice crystals are not pristine, but can either have some surface roughness of other non-idealities in their shape (Haapanala, 2017). We also simulate the radiance field near the sun to be able to retrieve the amount of diffuse radiation measured by a typical ground-based
instrument measuring the direct solar radiation (i.e. pyrheliometer). In the presence of ice clouds, the amount of diffuse radiation in the radiation measured by a pyrheliometer can be notable and lead to biases in cloud optical thickness that is retrieved from the measurement (Haapanala et al., 2017).

One of our main goals was to improve the treatment of dust optical properties in global aerosol-climate model by using spheroidal model particles (Merikallio et al., 2011) instead of spherical ones. However, our results show that the use of spheroidal model particles for dust optics has only small or moderate impacts on regional and global-scale direct radiative effects of dust (Haapanala, 2017). Consistent with this, experiments with a global aerosol–climate model indicate that the assumption of spherical shape for dust particles is not a considerable error source for climate models due to the compensating effects of dust nonsphericity (Räisänen et al., 2013, Haapanala, 2017). It is noted that this conclusion cannot be extended to remote sensing applications.

CONCLUSIONS

Modelling the solar radiative effects of atmospheric particles includes several challenging stages where approximations cannot be avoided. However, it is essential to avoid unnecessary simplifications where those are known to produce considerable errors in the results. Recent computational and methodological advances in light scattering and radiative transfer modelling have made it possible to use more morphologically faithful particle shape models in atmospheric radiation research, and the three dissertations (Haapanala, 2017; Merikallio, 2016; Lindqvist, 2013) summarised here demonstrate these advances all the way from morphologic modelling to light scattering computations and to radiative transfer modelling.

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REFERENCES


METHANE FLUXES FROM TREE STEMS IN A NUTRIENT RICH FORESTRY DRAINED PEATLAND IN SOUTHERN FINLAND

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INTRODUCTION

Methane (CH\textsubscript{4}) is among the most important greenhouse gases and its atmospheric mixing ratio is increasing (Hartmann et al. 2013). A few plant species living in wet conditions (e.g. rice and sedges) are found to be capable of transporting microbially produced CH\textsubscript{4} from anaerobic soil conditions to the atmosphere (Nouchi et al. 1990; Greenup et al. 2000). Boreal forests are commonly considered a net sink of atmospheric CH\textsubscript{4} due to CH\textsubscript{4} oxidizing bacteria (methanotrophs) in aerated soil layers (Topp and Pattey 1997; Kirschke et al. 2013). Recent studies have, however, demonstrated that also trees are capable of emitting CH\textsubscript{4} from their stems and shoots possibly by transporting anaerobically produced CH\textsubscript{4} from deeper soil layers to the atmosphere (Terazawa et al. 2007; Rice et al. 2010; Gauci et al. 2010; Pangala et al. 2015; Machacová et al. 2016). The transport of CH\textsubscript{4} within the tree is hypothesized to happen actively via transpiration stream (Pangala et al. 2015; Machacová et al. 2016) or passively via aerenchymatic tissues (Terazawa et al. 2015). Furthermore, tree leaves can be independent sources of CH\textsubscript{4} produced within the leaves in abiotic processes (Keppler et al. 2006). Thus it has become evident that trees might play an important role in the global CH\textsubscript{4} budget.

Current research of tree CH\textsubscript{4} fluxes covers principally the tropical and the temperate vegetation zones while studies in the boreal zone are scarce. In addition, high uncertainties remain in the mechanisms and the environmental factors behind the CH\textsubscript{4} emissions from trees. Research in the boreal vegetation zone is urgently needed in order to obtain understanding of the magnitude and both spatial and temporal variability in tree CH\textsubscript{4} fluxes, and to study the overall contribution of trees to the ecosystem CH\textsubscript{4} fluxes. This study aims to estimate the differences in the tree CH\textsubscript{4} fluxes between tree species and two different water supply conditions in a nutrient rich forested peatland in southern Finland.

METHODS

We measured forest floor and tree stem CH\textsubscript{4} exchange of three common boreal tree species at Lettosuo, a drained, nutrient rich peatland forest in Tammela, southern Finland (60\textdegree 38' N, 23\textdegree 57' E) during 7 June – 17 October 2016. The fluxes were measured by the static chamber technique at two different plots: a control plot and a partially harvested plot where all the Scots pine (Pinus sylvestris) trees (75% of the tree biomass) were removed to raise the water table level (WTL). The tree fluxes were measured from mature downy birch (Betula pubescens) and Norway spruce (Picea abies) at the control plot, and birch, spruce and pine at the partially harvested plot, from in total 25 sample trees (5 replicates/species/plot). Three birches from the partially harvested plot were selected to measure CH\textsubscript{4} flux variation within vertical profile of the stems. Characterization of microbial communities, quantification of methanogenic and
methanotrophic functional genes \((mcrA\) and \(pmoA\), respectively), and measurements of potential \(\text{CH}_4\) production and consumption from peat profile and forest floor moss samples were also carried out to obtain insight to the \(\text{CH}_4\) flux dynamics at the studied site.

RESULTS

At the partially harvested plot the WTL was generally 10–15 cm closer to soil surface compared to the WTL on the control plot, where the WTL depth was on average 55 cm during the growing season. Forest floor was a small sink of \(\text{CH}_4\) in both of the plots, although the \(\text{CH}_4\) uptake by soil was smaller at the harvested plot. We found small \(\text{CH}_4\) emissions from the stems of the trees at both of the plots, while occasional \(\text{CH}_4\) consumption also occurred (Fig. 1). Generally the \(\text{CH}_4\) emissions from the trees were higher and more dominant at the partially harvested plot compared to the control plot, and the fluxes were significantly different between the plots \((p < 0.001)\). The \(\text{CH}_4\) emission rates from the birches at the harvested plot decreased exponentially in the stem vertical profile (Fig. 2). Clear seasonal flux dynamics or significant differences in the \(\text{CH}_4\) flux between the species were not found at either of the plots. The laboratory incubation experiments showed that anaerobic \(\text{CH}_4\) production, \(\text{CH}_4\) oxidation potential (under 1000 ppm \(\text{CH}_4\)), and the amount of methanogens were higher in the peat of the partially harvested plot compared to the control plot.

![Figure 1. Box & whiskers plots of tree stem \(\text{CH}_4\) fluxes at partially harvested (top panel) and control (bottom panel) plots at Lettosuo in summer 2016, southern Finland. The top and the bottom of the boxes mark 25% and 75% percentiles and the whiskers show the range of entire flux data.](image-url)
CONCLUSIONS

The difference in the CH₄ flux rates between the control and partially harvested plots suggests that the WTL is a major regulator of tree CH₄ emissions on forestry drained peatlands, supporting our hypothesis that the CH₄ emitted by the stem originates from the soil. This hypothesis is further supported by the results of the peat incubation and microbial analysis indicating a higher CH₄ production potential at the partially harvested plot. Furthermore, the observation that more CH₄ is emitted from the lower part of tree stems compared to the upper part supports our hypothesis that most of the CH₄ emitted from tree stems is produced in the peat soil and transported to the atmosphere via trees.

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NEW PARTICLE FORMATION AT A RURAL BACKGROUND SITE IN WESTERN SAUDI ARABIA

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Keywords: aerosol particles, new particle formation, size distribution, aerosol shrinkage

INTRODUCTION

The Arabian Peninsula is one of the strongest aerosol particle source areas, both natural and anthropogenic, in the world. As a part of so-called dust belts, natural aerosol mass is dominated by desert dust, which can be transported over large distances (Prospero et al., 2002). Dust storms and episodes strongly change aerosol physical and optical properties causing strong perturbation into radiation-energy balance and air quality (e.g. Alam et al., 2014). Anthropogenic emissions mainly originate from road traffic, petroleum industry and local constructions (Khodeir et al., 2012). The size distributions, optical properties, and physico-chemical properties of aerosol particles are highly variable in such regions. In this study the physical properties of aerosols are, for the first time, comprehensively derived at a rural background area in Saudi Arabia. The study concentrates on aerosol number size distribution measurements, which reveal that atmospheric new particle formation events take place on clear majority of days in the region and that these events often show a shrinking mode mean diameter towards the end of the observed event. The shrinkage of newly formed aerosol particles has also been observed in other environments, but is so far not explained (Yao et al., 2010; Young et al, 2013; Salma et al., 2016).

METHODS

The Hada Al Sham site (21.802° North, 39.729° East, 254 m a.s.l.) is situated about 60 km east of the coastal city of Jeddah. The surroundings represent a rural area. The following in situ measurements are conducted at the station: PM₁₀₅ and PM₁₀ mass concentrations, total particle number concentration, particle number size distribution from 7 nm to 10 µm, aerosol black carbon concentration (absorption coefficient) and aerosol scattering coefficient. Cimel sunphotometer is used for measuring the columnar properties of the atmosphere. In addition, weather parameters are measured. More detailed description can be found from Lihavainen et al. (2016).

We analyzed aerosol size distribution data measured with a twin Differential Mobility Particle Sizer (DMPS) measuring from 7 nm to 850 nm in particle diameter over the measurement period from February 2013 to February 2015. The data coverage was around 64 %. New particle formation (NPF) event classification was done for the measurement days following the methods described by Dal Maso et al. (2005). NPF events were further separated into subclasses depending on whether they showed a clear shrinking mode during the later stages of the event or not. Particle growth and formation rates were determined for the NPF days as described by Kulmala et al. (2012) and air mass history was studied using a Lagrangian particle dispersion model FLEXPART version 9.02 (Stohl et al., 2005). European Centre for Medium-Range Weather Forecasts (ECMWF) operational forecast with 0.15 degree horizontal resolution, 137 vertical levels and 1 h temporal resolution was used as input data to FLEXPART.
RESULTS

The results of the Event classification are presented in Figure 1, which shows that NPF events are observed at the site very frequently (73% of all classified days) throughout the year, and that clear non-event days are extremely rare. Furthermore, approximately three quarters of the NPF days show shrinking, with a generally higher fraction of shrinking events occurring during the summer months. In Figure 2, we present an example of a NPF day that clearly illustrates the development of the mode mean diameter, turning from significant growth into shrinkage. The high frequency of NPF days is likely connected to the typically prevailing clear-sky conditions and high global radiation, in combination with sufficient amounts of precursor vapors for particle nucleation and growth. The median formation and growth rates for the event days were $8.7 \# / \text{cm}^3$ and $7.4 \pm 4 \text{ nm/h}$, respectively, both showing slightly higher values during the summer.

![Figure 1. Breakdown of the NPF event classification separately for each month and all of the 454 classified days combined.](image1)

![Figure 2. Particle number size distribution measured by DMPS showing a NPF event with a shrinking mode mean diameter (after 15:00) in Hada Al Sham October 2, 2013.](image2)

![Figure 3a shows the distribution of times for the different phases of the NPF events. The events usually start a few hours after the sunrise and last for ~9 h ending around the time of the sunset. The growth period typically lasts for around 6 h, while the shrinking period is shorter, beginning in the afternoon and lasting for around 3 h.](image3)
We assume that the particle shrinkage is caused by evaporation of semivolatile species under high ambient temperature and wind induced mixing, which both promote partitioning from the particle phase into the gas phase by increasing the saturation vapor pressure and by diluting the gas phase concentrations, respectively. This is supported by the higher fraction of shrinkage events observed during the warmer and more windy summer months (Figure 1), as well as by the typical onset time of shrinkage around the temperature and wind maxima (Figure 3 a, c and d). High temperature and increased wind speed are also often reported as the causes for particle shrinkage in previous studies on the subject, summarized in Alonso-Blanco et al. (2017).

The beginning of the NPF events is accompanied by a drop in the condensation sink (CS) and a shift in the wind direction from East towards West. These are most likely due to an increase in the boundary layer height and the onset of the sea breeze, occurring a few hours after the sunrise. The change in the wind direction results in polluted air masses from the large cities in the coastal area, which seems to be crucial for NPF at this site, as indicated by the air mass history analysis.
Figure 4. Average 24-hour footprint emission sensitivity for air masses arriving at the site during the time when NPF is typically taking place (10:00 LT) for a) event days and b) non-event days. The footprint emission sensitivity represents the amount of time the trajectories have spent over a certain grid point within the lowest 100 m above ground.

The average emission sensitivities (Figure 4 a and b) show, that the air masses arriving at the site during the typical time of NPF mainly originate from the coastal areas on event days, whereas on non-event days the source area points towards the inland. The atypical situation observed on non-event days is caused by strong Easterly winds that prevent the development of the sea breeze. This result clearly indicates the importance of the coastal emissions to the frequently observed NPF at this site.

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MOLECULAR DYNAMICS SIMULATIONS AND ISOTHERMAL HOMOGENEOUS NUCLEATION

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Keywords: HOMOGENEOUS NUCLEATION, MONTE CARLO, MOLECULAR DYNAMICS, LENNARD-JONES, CLUSTER.

INTRODUCTION

Two distinct molecular simulation techniques are usually used to predict the nucleation rates: Monte Carlo (MC) and molecular dynamics (MD) simulations. In MD the Newtonian equations of motion of interacting atoms or molecules are solved and hence the method allows directly the study of time-dependent cluster formation. In MC approach a thermodynamic property (in our case the work of cluster formation) is calculated by configurational sampling under some thermodynamic constraints. Using MC we obtain fully isothermal nucleation rate. Whereas in MD nucleation studies even applying thermostats do not bring system to completely isothermal conditions (Wedekind et al., 2007; Toxvaerd, 2016). In this study we compare the nucleation rates obtained with these two different approaches using Lennard-Jones interatomic potential.

METHODS AND RESULTS

The homogeneous nucleation process is directly observed in the large-scale molecular dynamics (MD) simulation procedure presented by Tanaka et al. (2011). Here the system is thermostatted with velocity scaling method, yet the cluster energy distribution deviates from the one corresponding to ambient temperature (Angélil et al., 2014; Wedekind et al., 2007; Toxvaerd, 2016). Influence of different thermostats on nucleation rate has been studied by Wedekind et al. (2007). The different thermostats appeared to affect similarly the nucleation rate except in the simulations with carrier gas as a coolant. Using nonisothermal nucleation theory they also extrapolated these results to higher concentration of the carrier gas when the completely isothermal conditions can be expected.

Contra MD, to calculate the nucleation rates via MC the time-independent results are supplemented to a classical treatment of cluster population dynamics. The classical kinetic model for the steady state nucleation rate can be expressed as the Becker-Döring sum

\[ J = \sum_{n=2}^{\pi} \frac{1}{\alpha_n N_n^{\text{eq}}} \left(\Delta W_n \right)^{-1}, \]

where \( \pi \) is larger than the critical cluster \( n^* \) (McDonald, 1963), \( \alpha_n \) evaporation rate of \( n \)-cluster and \( N_n^{\text{eq}} \) is the equilibrium cluster concentration determined as

\[ N_n^{\text{eq}} = N_1^{\text{eq}} \exp\left(-\frac{\Delta W_n}{kT}\right). \]

The work of cluster formation \( \Delta W_n \) is calculated by semigrand canonical Metropolis Monte Carlo method (Merikanto et al., 2004; Vehkamäki and Ford, 2000; Lauri et al., 2006). In the method
the grand canonical growth and decay probabilities are calculated for a single cluster at the time
and the cluster configuration space is traced out in a canonical Metropolis simulation. The average
growth and decay probabilities, $G_n$ and $D_n$, gained from the simulation have direct relation between
the condensation and evaporation rates in the Becker-Döring kinetic scheme and thus we can write
the work of formation of an $n$-cluster as

$$\Delta W_n = -kT \sum_{i=2}^{n} \ln \frac{G_{i-1}}{D_i}. \tag{3}$$

The MC simulation results can be easily scaled to obtain the work of formation at some other
monomer density, so for each temperature the simulation has to be performed only once. For MC
and MD to be comparable, we used identical Lennard-Jones potential and cluster connectivity
distances.

Instead of using the collision rates in Eq. (1) we are using the evaporation rates $\alpha_n$ obtained
by MD simulations in the microcanonical ensemble (the conserved quantities are $nVE$, where $V$
is volume and $E$ is energy)(Napari and Vehkamäki, 2006). Now the we are free from the crude
approximations of the kinetic gas theory which is typically used to estimate the collision rates.

Furthermore, the monomer depletion has to be taken into account because about 1% to 40% of the
molecules are clustered in the quasi-steady state of MD simulations. So, the unbalanced steady state
in calculations with MC data is driven to match the total number density of the MD simulations.

![Figure 1: Difference between the nucleation rates obtained by the MC and the MD simulations as
a function of the monomer density. The colored circles present the comparison with the MD results
by Tanaka et al. (2011) and Diemand et al. (2013). The arrows indicate cases where only the upper
limit for nucleation rate was derived. Black symbols shows the comparison with Wedekind et al.
(2007). Black squares and a circle refer to MD simulations with velocity scaling thermostat with
different time steps $\Delta t$. Crosses mark the comparison with the nonisothermal nucleation theory.](image-url)
The results of the comparison are presented in Figure 1. Most of the MD results demonstrate about 1–3 orders of magnitude lower nucleation rates than the ones obtained by MC simulations. Discrepancy between MC and MD with using velocity scaling thermostats is bigger for lower nucleating vapour concentrations and lower temperatures. There is good agreement of MC results with the points obtained by extrapolation to high carrier gas concentrations of MD results by Wedekind et al. (2007).

CONCLUSIONS AND FUTURE WORK

Application of MC simulation to nucleation studies implies the validity of the kinetic scheme and using such thermodynamic properties like free energy for small quasi-stable clusters. MD simulations are free from these assumptions even if the kinetic equation is used to calculate the nucleation rate. In that sense MD simulations can be considered as a “numerical experiment”, which can confirm or deny a theory. There is a good agreement between the theory and the “experimental” points shown as crosses in Figure 1, and we know that these points correspond to fully isothermal nucleation. For other points we have clear disagreement between MD and MC results. It has been mentioned (Yasuoka and Matsumoto, 1998; Wedekind et al., 2007) that usage of thermostats in MD simulations related to nucleation problems brings uncertain degree of thermalization. Our results support this idea. This problem grows with lowering down the nucleating vapour concentrations i.e. with approaching to real experimental conditions.

The only known reliable option is to use carrier gas as a thermostat in MD simulations studies of nucleation and hence our next goal is to carry out large-scale MD simulations with carrier gas to study homogeneous nucleation more carefully especially at lower, more realistic densities.

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REFERENCES


THE STUDY OF CONSTRAINED EQUILIBRIUM HYPOTHESIS IN NUCLEATION

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Keywords: NUCLEATION, CONSTRAINT EQUILIBRIUM, LENNARD-JONES, CLUSTER.

INTRODUCTION

Almost all theories of the vapour to liquid nucleation are based on well-known kinetic approach. The kinetic part of the theories comprise the solution of death-birth equations with two boundary conditions giving two different steady state solutions, which can be related to each other. The balanced steady state solution is identified with equilibrium cluster distribution and this is crucial assumption sometimes called constrained equilibrium hypothesis (CEH). The validity of CEH was questioned many times (Lushnikov and Kulmala, 1998; Barrett, 2002; Ford and Harris, 2004; Bartell, 2009). The citation list is not full, and, perhaps, even the authors of the kinetic approach were in doubts equalising the balanced steady state to conditions for equilibrium. However it was the only way to advance in nucleation theory at that time. Nowadays the computer simulations can help in studying the validity of CEH. It has been reported about the break of CEH (Zhuo, 2005) in MD simulations of argon nucleation. In our opinion it is not possible to deduce from those simulations about the brake of CEH. They rather demonstrate that evaporation and condensation rates are different in balanced and unbalanced steady states. That is not surprising since the conditions of the simulations were at the vapour densities close to the liquid ones, so the process can hardly be called vapour to liquid nucleation. In the present study we carefully examine the assumptions involved in the basis of the nucleation theories. Particularly we study the conditions of the kinetic scheme applicability and limits when CEH can be used. The Lennard-Jones vapour is used as an example.

RESULTS AND DISCUSSION

Suppose we have ensemble of \( n\)-clusters where their energy \( E\) is distributed according to normalized function

\[
\varphi(E) = \frac{1}{N_n} \frac{dN_n(E)}{dE},
\]

(1)

where \( N_n(E) \) is the number of \( n\)-clusters with energy less than \( E\), \( N_n \) is the total number of \( n\)-clusters. We section the distribution function in equal narrow energy interval \( \Delta E \) and label them with \( i\) index, so the number of cluster with energy \( E_i \) equals to

\[
\Delta N_{n,i} = N_n \varphi(E_i) \Delta E.
\]

(2)

The clusters evolution with time \( t\) is described by death-birth kinetic equations

\[
\frac{\partial \Delta N_{n,i}}{\partial t} = \alpha_{n+1\rightarrow i} N_{n+1} + \beta_{n-1\rightarrow s} N_{n-1} - (\alpha_{n,i\rightarrow} + \beta_{n,i\rightarrow}) \Delta N_{n,i} - \sum_k (\gamma_{n,i\rightarrow k} \Delta N_{n,i} - \gamma_{n,k\rightarrow i} \Delta N_{n,k}),
\]

(3)
where $\beta$ is the monomer condensation rate, $\alpha$ is the evaporation rate, $\gamma_{n,i\rightarrow k}$ is a rate of transition for the $n$-cluster from energy $E_i$ to $E_k$ induced by collision with carrier gas molecules, in the indexes of evaporation and condensation rates the sharp end of the arrow points out the final energy value of transition and the blunt end of the arrow shows the initial one. If one of them is not specified it means that the quantity is integral and evaporation/condensation occurs to or from all possible energy values. Knowing all the coefficients in Eq. (3) provides the possibility to calculate nucleation rate.

To obtain the condensation rates, the collision cross section (CCS) between the cluster and the monomer is geometrically estimated by a simple brute-force Monte Carlo method. We consider each atom of a cluster as a sphere with radius $r$, and the cluster is association of such spheres. The random trajectories of colliding monomers are produced by generating two random points on a sphere with a radius larger than $r_{ref}$ serving as a reference surface area measure. The line between these two points is the axis of a cylinder with radius $r$. The corresponding hits are counted if the cylinder has an intersection with the reference sphere or the cluster. The possible intersection can be calculated by basic vector calculus: if the distance from a cluster point to the line is less than $r$ the monomer hits the cluster. Several thousands of random trajectories are generated in order to get good statistics. The results are presented in Figure 2.

The evaporation rates are obtained though (MD) simulations. The examples of the results are presented in Figure 1. The transition rates $\gamma_{n,i\rightarrow k}$ are calculated assuming that that the carrier gas atoms elastically collide with the cluster atoms. The calculations of CCS have free parameter $r$. To define it we consider the system at formally infinitely high concentrations of the carrier gas. According to general principle of Statistical Mechanics the carrier gas serving as a thermostat brings all the cluster to equilibrium in this case. Therefore the balanced steady state solution of Eqs. (3) must satisfy Boltzmann distribution. In other words, the detailed balance in the following form must hold

$$N_n \int_{-\infty}^{\infty} \beta_n(E)\varphi_n(E)dE = N_{n+1} \int_{-\infty}^{\infty} \alpha_{n+1}(E)\varphi_{n+1}(E)dE,$$

where $\varphi_n(E)$ has the energy distribution corresponding to the Boltzmann one. As a matter of fact, to satisfy Eq. (4) radius $r$ appears to have reasonable value for cluster sizes higher than 10 (Figure 2).
Figure 2: Collision cross section as a function of cluster size obtained with the brute-force Monte Carlo method (solid line) for $r = 2.5$ Å. The dashed line corresponds the collision cross section of spherical cluster with bulk liquid density of argon at 50 K.

3. For smaller clusters the collision cross sections demonstrate unusual growth despite the fact we have not observed any peculiarity in geometrical size from brute-force

Figure 3: Collision cross section as a function of cluster size obtained from the detailed balance equation

Monte Carlo method (Figure 2). The cluster with size smaller than 10 and in the segment of high energies evaporate with a rate (Figure 1) comparable with a period of intermolecular vibrations of the cluster. Therefore to save the date balance we have to assume unusually big CCS. On the hand, if the group of the molecules with a high energy is not counted as a cluster than we cannot satisfy Boltzmann distribution for these particular cluster sizes. This inconsistency demonstrate the problem in using CEH in nucleation theory.
CONCLUSION

The combined molecular dynamics and Monte Carlo study of the Lennard-Jones argon clusters demonstrate that it is necessary to assume growth in surface area with decreasing of number of atoms for the clusters’ sizes smaller than 10. Otherwise the detailed does not hold. The same clusters evaporate with a rate comparable with a period of intermolecular vibrations. Discarding these clusters allows us to save the detailed balance, but then the Boltzmann distribution is not satisfied. This makes constrained equilibrium hypothesis inapplicable to nucleation.

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REFERENCES


AEROSOL CHEMICAL COMPOSITION IN- AND OUT-OF- CLOUDS IN FINLAND

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Keywords: CLOUD EVENTS, CHEMICAL COMPOSITION, AEROSOL MASS SPECTROMETER

INTRODUCTION

One of the largest uncertainties in our understanding of human-caused climate change is associated with the aerosol effects on clouds. Anthropogenic activities have led to an increase in the atmospheric aerosol concentrations. A subset of aerosol particles can act as cloud condensation nuclei (CCN), meaning a particle that can form a cloud droplet at a certain level of water vapour supersaturation. Elevated concentrations of CCN can increase the number concentration of droplets in a cloud but decrease their mean size (e.g. Komppula et al., 2005; Portin et al., 2009). Because of these, clouds will be optically thicker, and the formation of precipitation might be delayed leading to increase in the lifetime of clouds in some situations (Twomey, 1974; Albrecht, 1989). In order to reduce the uncertainty of climate impact of aerosols, a more complete understanding on how particles form droplets is required (IPCC 2013).

Individual cloud droplets initially start their life as aerosol particles. Thus, it is critical to understand what determines the particle’s ability to form cloud droplet in the atmosphere under various conditions. Theoretical and experimental efforts have been set to investigate the particle’s activation ability for decades. Particle size seems to be a more important determinate of CCN variations than chemical composition in some cases (e.g. Dusek et al., 2006), while for the real atmospheric aerosol populations where the chemical composition is size-dependent, the ability of aerosols to serve as CCN is getting more complicated. Less is known about the link between aerosol chemical composition and potential to act as CCN behaviours.

METHODS

One campaign for the observation of cloud events was carried during Oct. 10-Nov. 29, 2016 in Puijo Cloud Experiment 2016 campaign (PuCE2016). The observation station is located on the top of Puijo tower in Kuopio (Portin, et al., 2009, Leskinen et al., 2009). A cloud event was considered to take place at Puijo when the visibility at the top of the tower dropped below 200m. Totally, 22% of time was observed by clouds in the campaign. An Aerodyne high resolution aerosol time-of-flight mass spectrometer (TOF-AMS) was used to measure the chemical composition of cloud particles (DeCarlo et al., 2006). In order to separate contributions of organic nitrate and inorganic nitrate to aerosol chemical composition during the cloud event, we also performed positive matrix factorization (PMF) analysis on the high resolution mass spectra (Ulbrich et al., 2009). Supporting measurements on the aerosol, gas and meteorological parameters were also made.
RESULTS AND DISCUSSION

For nitrate aerosol components, organic nitrate account for 19.9% of total nitrate aerosol mass concentration, whilst ammonium nitrate (inorganic nitrate) dominated the rest of nitrate components during the cloud periods (panel A, Figure 1). In contrast, during cloud-free periods, the mass fraction of organic nitrate to the total nitrate mass was 42.2% and inorganic nitrate of 57.7%.

![Figure 1](image1.png)

Figure 1. The mass fraction of nitrate aerosol components in presence of organic and inorganic chemical forms in (panel A) and out of (B) cloud periods.

Figure 2 show the ratio of predicted to the measured ammonium aerosols during cloud and cloud-free periods. The predicted NH$_4^+$ mass loading is the amount needed to fully neutralize the anions that were measured (Zhang et al., 2007):

\[ \text{NH}_4^+\text{,pre} = 18 \times \left( 2 \times \text{SO}_4^{2-} / 96 + \text{NO}_3^- / 62 + \text{Cl}^- / 35.5 \right) \]  

(1)

where NH$_4^+$, SO$_4^{2-}$, NO$_3^-$ and Cl$^-$ represent the mass concentrations (in µg m$^{-3}$) of the species and the denominators correspond to their molecular weights. Factor 18 is the molecular weight of NH$_4^+$.

The ratios of those two components in cloud and cloud-free periods were 1.1 and 1.4, respectively, suggesting the aerosol during cloud periods was more neutralized than cloud-free periods. Table 1 shows the distribution of sulfate species in and out of cloud, verifying our conclusions.

![Figure 2](image2.png)

Figure 2. The ratios of predicted to the measured ammonium in and out of cloud periods.
Table 1 The mass concentration of neutralized and acidic sulfate species in and out of cloud period in this campaign.

<table>
<thead>
<tr>
<th>Species</th>
<th>µg m⁻³ in cloud periods</th>
<th>µg m⁻³ out of cloud periods</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.78±0.65</td>
<td>1.05±0.98</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>0.04±0.12</td>
<td>0.60±0.83</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.00±0.00</td>
<td>0.04±0.12</td>
</tr>
</tbody>
</table>

Figure 3 shows the correlations of secondary organic aerosol (LVOOA+SVOOA) to sulfate species. A better correlation was observed during cloud periods than cloud-free periods, indicating the aqueous chemistry might place a role in affecting the SOA formation in the campaign.

CONCLUSIONS

Our preliminary results show the distinct difference of aerosol chemical composition during cloud periods and cloud-free periods. The difference can be explained by the partitioning of ammonia in and out of cloud droplets, aqueous chemistry and possible wind direction. More data analysis is needed for better interpretations on the results.

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Impact of aerosol acidity on organic nitrates formed from α-pinene ozonolysis

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Keywords: SOA, organic nitrates, particulate organic nitrates, aerosol acidity, AMS, FIGAERO

INTRODUCTION

Secondary organic aerosol (SOA) accounts for a significant fraction of aerosols, worldwide (e.g. Hallquist et al., 2009). It originates from the oxidation products of volatile organic compounds (VOCs) that are emitted both from biogenic and anthropogenic sources. The most abundant biogenic VOCs emitted from the biosphere are isoprene and monoterpenes, such as α-pinene. They form SOA in different ways. Isoprene-derived-SOA has been mainly explained through acid catalyzed reactive uptake of isoprene epoxy diols (IEPOX) that are formed from the oxidation of isoprene under low- and high-NOx conditions (Surratt et al., 2010) whereas a significant fraction of α-pinene-derived-SOA forms through the condensation of low-volatility organic vapors (highly oxygenated molecules, HOMs) arising from the oxidation of α-pinene (Ehn et al., 2014). Nitrogen monoxide, NO, can impact the oxidation of the biogenics by the formation of gaseous organic nitrates (ONs) with relatively high volatilities. These products can also contribute to the formation of SOA (as particulate organic nitrates, pONs) that are worldwide observed in the particle phase (e.g. Kiendler-Scharr et al., 2016, Lee et al., 2016). The lifetime of pONs, however, is estimated to be short, only a few hours (Lee et al., 2016). The short life time could be due to pON hydrolysis, that might be acid catalyzed (e.g. Rindelaub et al., 2015). The decomposition products of pONs could also impact the NOx cycle. In this study, we want to investigate both the acid catalyzed reactive uptake of α-pinene oxidation products and the possibility of acid catalyzed particle phase processing involving the pONs.

METHODS

This study was conducted in the COALA-chamber which is a 2m³ Teflon chamber operated in a continuous flow mode under room temperature and atmospheric pressure with a residence time of 50 minutes. 30 ppb of α-pinene, 80 ppb of ozone and 30 ppb of NO2 were injected into the chamber. The chamber was equipped with LED-lights (λ = 400 nm) that were used to photolyze NO2 in order to generate NO. The NO concentration was either 100 or 200 ppt. Low-NOx experiments were also conducted where no NO2 was added to the chamber. The RH in the chamber was either < 1% or ~45%. 80 nm size selected sulfate seed aerosols were injected into the chamber. They were either “non-acidified” ammonium sulfate (AS) aerosols or “acidic” ammonium bisulfate (ABS) aerosols.

Seed aerosols were either injected directly to the dry chamber (AS dry/ABS dry conditions) or exposed to a humidity higher than 80% to receive deliquesced aerosols with higher aerosol liquid water (ALW) content (AS deli /ABS deli conditions). Under dry conditions, the ABS is deliquesced due to its acidity and has therefore a minor ALW content whereas the AS is injected as a crystal. Under the humid conditions, both seed types are deliquesced with approximately the same ALW content.

In chamber studies, the isoprene-derived-SOA formation through acid catalyzed reactive uptake of IEPOX has been observed to be most efficient when the relative humidity is low. Since the seed aerosols are often chosen to be either AS or ABS, their water contents are different, even at low humidities. This motivated us to explore the impact of acidity also under humid conditions keeping in mind that the acidity of the
particle will be diluted with a higher ALW content that could slow down the reactive uptake of gas phase products and/or the particle phase processes.

The measurements were mainly done in real time. α-pinene and its oxidation products were measured using a Proton Transfer Reaction Time-of-Flight mass spectrometer (PTR-ToF) and Chemical Ionization Mass Spectrometers using iodide and nitrate adducts (I-CIMS and NO$_3$-CIMS). The particle phase was measured with an Aerosol Mass Spectrometer (AMS) and a Filter Inlet for Gases and AEROsols (FIGAERO) deployed in front of the I-CIMS. Also the aerosol volatility was measured with a Volatility Tandem Differential Mobility Particle Analyzer (V-TDMA) and the aerosol size distribution was recorded with a Differential Mobility Particle Sizer (DMPS).

**RESULTS**

The aerosol acidity enhances SOA formation. In the dry chamber the SOA mass concentration was more than a double with the acidic ABS seed compared to the non-acidified AS seed. When the ALW was added to the particles the differences in SOA mass concentrations were negligible, which was likely due to the ALW diluting the aerosol acidity and thus slowing down the heterogeneous processes.

---

**Fig. 1.** A) The total nitrate mass concentration (a large fraction is pON) measured by the AMS under different NO concentrations, B) The total nitrate mass concentration divided by the total organic mass concentration measured by the AMS, C) The contribution of C$_7$ to C$_{10}$ pON to the total signal between $m/z$ 200 and 600 Th. The color coding is the same in figures A-C. Acidic ABS seed in a dry chamber condition is shown in purple, the humidified ABS in a humid chamber is shown with purple stripes, neutral AS seed in a dry chamber is in blue and humidified AS seed in a humid chamber is shown with blue stripes.

Also the pON concentration in the particles was highest for the dry ABS case (Fig. 1A). pONs were detected with the FIGAERO-I-CIMS and the AMS. Since the AMS uses electron impact ionization (70 eV), only little molecular information is preserved. The fragmentation of pON, however, differs from the
inorganic nitrate fragmentation pattern: the ratio between NO$^+$ and NO$_2^+$ ions is high (>5) for pON and low (2 – 3) for inorganic nitrates. In these experiments the NO$^+$:NO$_2^+$-ratio was found to be around 6 throughout the experiments indicating that a large fraction of the nitrates were organic.

The ratio between the total nitrate mass concentration and the total organic concentration was lowest both for the ABS dry and ABS deli (Fig. 1B) which was likely due to particle phase processing of pON. This hypothesis was motivated by the Fig. 1C showing the contribution of C$_7$ to C$_{10}$ pON to the total signal between $m/z$ 200 and 600 Th measured by the FIGAERO-I-CIMS. Lower C$_{10}$ contributions to the total signal in the acidic particles compared to the neutral ones was observed. Also, slightly bigger contributions of smaller pONs, e.g. C$_7$ and C$_8$ compounds, to the total was observed with the acidic particles. This could be due to the decomposition of pONs leading to smaller molecules that could eventually evaporate to the gas phase. The analysis of the gas phase N-containing species is on-going.

Preliminary results of nitric acid, both in the gas and particle phases, reveal an acidity dependence that could indicate that nitric acid is a possible decomposition product of the pONs. More detailed analysis on the gas phase data could give us more insights of the fate of pONs.

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REFERENCES


GREENHOUSE GAS FLUXES ON ADJACENT WETLAND, LAKE AND FOREST ECOSYSTEMS WITHIN A SUBARCTIC CATCHMENT

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Keywords: GREENHOUSE GAS, CATCHMENT, UPSCALING, EDDY COVARIANCE

INTRODUCTION

The Finnish Meteorological Institute has been running a micrometeorological measurement station at Kaamanen in northern Finland since 1997. These measurements of the ecosystem-atmosphere exchange of energy and greenhouse gases (GHGs) have been conducted at a wetland site using the eddy covariance (EC) method (Aurela et al., 2002, 2004). In 2017, EC flux measurements were also started at adjacent lake and forest sites. In addition, GHG fluxes were measured with the chamber technique.

The ecosystem-atmosphere exchange of CO₂ and CH₄ were measured during the summer 2017 on adjacent wetland, lake and forest ecosystems as part of the CAPTURE -project (Carbon dynamics across Arctic landscape gradients: past, present and future) funded by the Academy of Finland. The objective of these particular measurements was to observe the growing season carbon fluxes on these ecosystems and habitat types, e.g. on different land cover classes (LCCs) of the wetland. Using these data, the annual ecosystem-level GHG balances will be determined and upscaled to a catchment scale and further to a regional scale. This will be achieved by combining the EC flux measurements with the LCC specific fluxes from the chamber measurements and a detailed vegetation mapping based on satellite data and field measurements.

METHODS

The Kaamanen wetland is a mesotrophic flark fen (N69°8.435', E27°16.189, 155 m a.s.l.) comprising dry strings and wet flarks. The lake within the catchment is shallow (< 1 m) clear water lake and it is located 200 m southwest of the wetland site. The Scots pine forest, located 300 m west of the wetland site, has a mean tree height of 11 m (Figure 1). The EC measurement systems consisted of a sonic anemometer (METEK USA-1 at all sites), a CO₂ analyzer (LI-COR LI-7000 at wetland and forest; Picarro 2311-f at lake) and a CH₄ analyzer (LGR RMT-200 at wetland; Picarro 2311-f at lake). The measurement heights were 14 m, 5 m and 2 m at the forest, wetland and lake site, respectively.

The three EC towers provide continuous data from the main ecosystems of the area enabling the integration of GHG fluxes over the whole catchment. Flux chamber measurements add more detail to the areally averaged data obtained from the EC measurements, as the vegetation distribution within the catchment can be taken into account more precisely with the multiple chamber measurements conducted on different LCCs.
Vegetation and land cover classes were mapped in detail around the EC towers during the summer 2017. The mapping consisted of plant species coverage observations, soil sample collection and pH measurements along transects.

Manual chamber flux measurements were conducted by a Picarro G2401 gas analyzer on 17 locations at the wetland and 5 locations at the lake site. At the wetland, the chamber measurements were divided into four different vegetation classes that characterize the mesotrophic flark fen (Maanavilja et al., 2011). Across the microtopographical gradient there were five collars within the Sphagnum moss and dwarf birch-dominated low string margins, four collars within flarks with Trichophorum tussocks, four collars with sedge and brown moss vegetation and four collars on the clearly elevated dry strings, respectively. At the lake site, the chamber measurements were done at two collar positions on the shore above the water level and with two collars below the water level, respectively, and on a floating rig positioned towards the centre of the lake.

![Figure 1: Preliminary land cover class map of the area, with the EC tower locations shown with stars. The LCC map is classified from the WorldView2 image acquired on 6 June 2013, copyright Digital Globe, and has a pixel size of 2 m. The black ovals represent isolines of the modelled flux footprint demonstrating the spatial scale of the EC measurements.](image)

RESULTS AND CONCLUSIONS

Four sets of chamber measurements were taken during the growing season (June – August) in 2017 (Figure 2). The measurements had a 2-min chamber closure time, and three different radiation levels (no cover, half cover and full cover) were applied. The vegetation types and leaf area index (LAI) were specified for each measurement. At the fen, the ecosystem-atmosphere GHG exchange measured with the chambers was compared with the EC flux measurements.
Both measurement methods utilized gave similar GHG fluxes at the fen (Figure 2). The CO$_2$ flux measured with the EC method indicated slight net ecosystem respiration (positive sign in the graph) at the start of the growing season, which changed to net ecosystem uptake at a level of -0.20 mg CO$_2$ m$^{-2}$ s$^{-1}$ (negative sign in the graph) during July 2017. In July, the fluxes of ecosystem net uptake measured by chambers were somewhat smaller than the EC-based estimate. There was significant variation in the CH$_4$ fluxes among different LCCs, and the spatially integrated EC fluxes were within this variation. For a proper comparison, it will be necessary to consider the footprint of EC measurements and spatial representativeness of the chamber plots.

The fen and forest sites show similar diurnal cycles of CO$_2$ flux, with the forest however showing larger net respiration and uptake (Figure 3). As the EC tower at the lake site is located on the northern shore of the lake, the measured fluxes reflect the changing fetch as the wind direction changes from the south to the north.

![Figure 2: EC and chamber flux timeseries of CO$_2$ and CH$_4$ measured at the fen during the growing season in 2017. Chamber fluxes are represented for each of the four vegetation types. Total ecosystem respiration (TER) values were obtained by fully covering the chamber and measuring the flux. Gross primary productivity (GPP) was obtained by subtracting TER with Net ecosystem exchange (NEE).]
Figure 3: CO\textsubscript{2} and CH\textsubscript{4} eddy covariance fluxes measured at the lake, wetland and forest sites during the first week of July 2017. Wind direction and air temperature are also shown in the figure. The lake EC tower is located at the northern shore of the lake. At the forest EC tower the fetch area covers forest ecosystem while the wind sector is between west and north.

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REFERENCES

AMBIENT AIR BVOC MIXING RATIOS ARE HIGHLY DEPENDENT ON TEMPERATURE

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INTRODUCTION

Isoprene, monoterpenes (MTs) and sesquiterpenes (SQTs) are the main biogenic volatile organic compounds (BVOCs) emitted from the boreal forest. They are known to influence chemical communication by plants and insects, the oxidation capacity of air and particle formation and growth. In the air BVOCs readily react with atmospheric oxidants, and the photochemical oxidation of even small organic compounds can lead to the formation of tens to hundreds of first generation products, which then undergo further oxidation and transformations (Glasius and Goldstein, 2016). Thus, atmospheric chemists will probably never be able to identify all oxidation products of all VOCs in the atmosphere. Therefore, detailed knowledge on the primary emitted compounds is crucial.

Data sets on mixing ratios of individual MTs and especially SQTs are scarce and often only from short measurement campaigns. In this study ambient air measurements of VOCs were conducted in 2011, 2015 and 2016 at SMEAR II site in Hyytiälä with in situ gas chromatograph – mass spectrometers (GC-MSs). VOC measurements are laborious and complex and even with this intensive campaigns, data does not cover all periods continuously. To be able to parametrize the mixing ratios and fill the gaps in the data, we studied temperature dependence of mixing ratios. Temperature is known to be major factor controlling the emissions of these BVOCs from local trees (e.g. Tarvainen et al. 2005, Hakola et al. 2006 and 2017).

METHODS

Mixing ratios were measured with three different in situ thermal desorpter-gas chromatograph-mass spectrometers (TD-GC-MSs). In 2015 and 2016 two different GC-MSs were used in parallel.

GC-MS1 was used for the measurements of isoprene and individual monoterpene (MTs) in Jan-Oct 2011 and May-Jul 2015. One 60-min sample was collected in the cold trap of thermal desorption unit (ATD-400, PerkinElmer) every other hour and analyzed in situ with a gas chromatograph (HP 5890, Agilent Technologies) with DB-1 column (60m, id. 0.25 mm, ft. 0.25 µm) and a mass selective detector (HP 5972, Agilent Technologies). Measurements with GC-MS1 have been described in detail by Hakola et al. (2012).

GC-MS2 was used for the measurements of MT sum in May-Oct 2015 and Feb-Sep 2016. Samples were taken every other hour. The sampling time was 60 min. Samples were analyzed in situ with a thermal desorption unit (Unity 2 + Air Server 2, Markes International LTD, Llantrisant, UK) connected to a gas chromatograph (Agilent 7890A, Agilent Technologies, Santa Clara, CA, USA) and a mass spectrometer (Agilent 5975C, Agilent Technologies, Santa Clara, CA, USA). Since the instrument was also used for measurements of alcohols and volatile organic acids, a polyethylene glycol column, the 30-m DB-WAXetr with an inner diameter of 0.25 mm and a film thickness of 0.25 µm, was used for the separation. The method has been described in more detail by Hellén et al. (2017).
GC-MS3 was used for the measurements of individual MTs, SQTs and isoprene in Arp-Nov 2016. With GC-MS3 air was drawn at the flow rate of 1 l min\(^{-1}\) through a 1m long fluorinated ethylene propylene (FEP) inlet (id. 1/8 inch) and for ozone removal through a 1m long heated (120°C) stainless steel tube (od. 1/8 inch, Hellén et al. 2012a). VOCs were collected from a 40 ml min\(^{-1}\) subsample flow(?) in the cold trap (Carbopack B/Tenax TA) of the thermal desorption unit (TurboMatrix, 650, Perkin-Elmer) connected to a gas chromatograph (Clarus 680, Perkin-Elmer) coupled to a mass spectrometer (Clarus SQ 8 T, Perkin-Elmer). A HP-5 column (60m, id. 0.25mm, film thickness 1 µm) was used for separation.

Monthly means were calculated for all available data for each month. Daily means were calculated for days with no missing data points starting at 8:00 (UTC+2) and ending at 8:00 (UTC+2) next day.

RESULTS

Monthly means of MT mixing ratios in 2011, 2015 and 2016 have very strong exponential correlation with temperature (R\(^2\)=0.92, Figure 1a). Considering only data from 2016 (Apr-Nov), which had the best quality, the correlation is even higher (R\(^2\)=0.96). Correlation of photosynthetic active radiation (PAR) with monthly mean MT mixing ratios was also high (R\(^2\)\text{Apr-Nov 2016}=0.73), but clearly lower than with temperature. The site is dominated by Scots pines, which are known to have temperature and light dependent emissions of MTs (Tarvainen et al. 2005). Also daily means of MTs correlate with temperature (R\(^2\)\text{Apr-Nov 2016}=0.83 and R\(^2\)\text{Jun-Aug 2016}=0.88). High correlation of mean mixing ratios with temperature indicates that main factor controlling the seasonality of the emissions is meteorology. In an earlier study by Lappalainen et al. (2009) lower correlation (R\(^2\)=0.50) with temperature was found for PTR-MS data measured at this same site. However, they used only day-time medians and mixing ratios are generally higher during the nights. In our study 24-hour averages was used.

Figure 1. Correlation of temperature with a) monthly mean MT mixing ratios measured in 2011, 2015 and 2016 and b) monthly mean SQT mixing ratios measured in 2016 at SMEAR II site in Hyytiälä.
Temperature dependence of monoterpene emissions is often described by the Guenther algorithm (Guenther et al., 1993):

\[ E = E_S \times \exp(\beta (T - T_S)) \]

where \( E_S \) is the standardized emission rate (µg gdw\(^{-1}\) h\(^{-1}\)), \( T \) is the leaf temperature (°C), \( T_S \) is the standard temperature of 30 °C and \( \beta \) is the temperature sensitivity (°C\(^{-1}\)) of emissions. Often \( \beta \)-value 0.09 °C\(^{-1}\) is used to describe monoterpene emissions. In our monthly and daily mean mixing ratio data temperature sensitivity is clearly higher (\( \beta \geq 0.20 \) °C\(^{-1}\), Figure 1 and Table 1). However, \( \beta \)-value of emissions is known to vary with season and tree species. Here temperature sensitivity of daily mean MT mixing ratio for summer months (\( \beta = 0.27 \) °C\(^{-1}\), Jun-Aug) was higher than for the whole growing season (\( \beta = 0.20 \) °C\(^{-1}\), Apr-Nov). Temperature affects also vertical mixing of air and lower mixing after warm sunny days is one probable reason for increased temperature sensitivity of mixing ratios.

<table>
<thead>
<tr>
<th></th>
<th>Daily means (Jun-Aug 2016)</th>
<th></th>
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<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>a</td>
<td>MRT20 (pptv)</td>
<td>( \beta ) (°C(^{-1}))</td>
<td>( R^2 )</td>
</tr>
<tr>
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<td>0.18</td>
<td>0.84</td>
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<tr>
<td>SQT sum</td>
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<td>108</td>
<td>0.49</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 1. Intercept (a) of temperature dependence curve, mixing ratio at 20 °C (MRT20) calculated from the curve, temperature sensitivity (\( \beta \)) and correlation (\( R^2 \)) of daily (Jun-Aug) mean mixing ratios with temperature measured at SMEAR II in 2016. Fitted curves were exponent functions \( y = ae^{bx} \), where \( y \) = mixing ratio and \( x \) = temperature.
To study the temperature sensitivity of individual MTs, data from GC-MS3 was used. Exponential correlation of daily means of individual MTs with temperature was found to be high for most MTs (Table 1). As for the MT sum, daily means of individual compounds have also higher correlation with temperature and higher temperature sensitivity during summer months (Jun-Aug) compared to the whole measurement season (Apr-Nov). Of the MTs limonene had the highest correlation and highest temperature sensitivity ($R^2=0.91$, $\beta=0.34 \, ^\circ\text{C}^{-1}$). and $p$-cymene did not show any correlation with temperature ($R^2=0.07$, Table 1). $p$-Cymene has been detected in spruce emissions (e.g. Hakola et al. 2017), but it is also known to have anthropogenic sources (Hakola et al. 2012).

Due to the high reactivity of SQTs, their ambient mixing ratios are very low even if their emissions are high. Of the used instruments only GC-MS3 was able to detect these very low mixing ratios and therefore SQT data is available only for the year 2016 (Apr-Nov). Of the SQTs $\beta$-caryophyllene had the highest mixing ratios, but in summer also longicyclene, $\beta$-farnesene and 4 unidentified SQTs were detected. As for the MTs, monthly and daily means of SQTs had very strong exponential correlation with temperature (Figure 1b, Table 1). Temperature sensitivity of SQTs was even higher than for MTs. SQT emissions are known to be temperature and possibly also light dependent (Duhl et al. 2008). Especially $\beta$-caryophyllene mixing ratios had very high correlation with temperature ($R^2>0.95$) indicating only temperature dependent emissions. Also monthly means of the SQT sum had very high exponential correlation with temperature ($R^2=0.97$, Figure 1b) indicating that seasonality is driven by the temperature. However, for other SQTs than $\beta$-caryophyllene correlation was lower and other factors for example light and stress may also have significant effect. $\beta$-Farnesene is known to be emitted due to biotic stress (Kännaste et al., 2008) and it has been shown to increase simultaneously with linalool in the emissions of Spruces and Scots pines (Hakola et al. 2006 and 2017). However, in our mixing ratio data they did not correlate.

Isoprene emissions are known to be both light and temperature dependent. Here correlation of isoprene daily mean mixing ratios with light and temperature activity factor ($\text{CL}^*\text{CT};$ Guenther et al. 1993) was a bit lower ($R^2=0.74$) than for the only temperature ($R^2=0.84$).

**CONCLUSIONS**

Temperature is a major factor controlling mixing ratios of BVOCs in the air of boreal forest. Both monthly and daily mean mixing ratios of MTs have very strong exponential correlation with temperature ($R^2=0.92$ and $R^2=0.88$). MTs with lower correlation have lower mixing ratios and are known to have also other sources than temperature controlled emissions from local trees.

Kotkanen et al. (2016) have developed MT proxies, which are used for calculating mixing ratios of the MT sum at the SMEAR II. The proxies are based on the temperature-controlled emissions from the forest ecosystem, the dilution caused by the mixing within the boundary layer and different oxidation processes. However, our data shows that monthly and daily means of both sum and individual MT mixing ratios can be described also just by temperature.

At the moment there is very little knowledge on SQT mixing ratios in the air and also emission data is much sparser than for MTs. Based on our results SQT mixing ratios are strongly dependent on temperature and have even higher temperature sensitivities than MTs. Even though isoprene emissions are known to be both light and temperature dependent, higher dependence of mixing ratios only on temperature was found.
ACKNOWLEDGEMENTS

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CONCENTRATIONS OF VOLATILE ORGANIC AMINES IN AMBIENT AIR OF BOREAL FOREST

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INTRODUCTION

Amines are gaseous bases, whose general formula is RNH₂, R₂NH or R₃N. The most common and abundant amines in the atmosphere are low-molecular-weight aliphatic amines containing one to six carbon atom, such as monomethylamine (MMA, (CH₃)NH₂), dimethylamine (DMA,(CH₃)₂NH), trimethylamine (TMA, (CH₃)₃N), ethylamine (EA, (C₂H₅)NH₂), diethylamine (DEA, (C₂H₅)₂NH) and triethylamine (TEA, (C₂H₅)₃N) (Ge et al., 2011). These amines have sources that are both anthropogenic (e.g. combustion, biomass burning and animal husbandry) and biogenic (oceans, soil and vegetation) (Ge et al., 2011). Models have shown that they could affect aerosol particle formation with sulfuric acid even at very low mixing ratios (Kurtén et al. 2008, Paasonen et al. 2012). Amines also affect hydroxyl radical (OH) reactivity and therefore atmospheric chemistry (Hellén et al. 2014).

Studies of the atmospheric concentrations of amines are scarce, and most of them are based only on short campaigns. The in-situ method developed in this study for atmospheric amine measurements was used in the boreal forest, where amines are expected to affect aerosol particle formation even at extremely low concentrations (Kurtén et al. 2008, Paasonen et al. 2012). We report seasonal and diurnal variations of amines in boreal forest air and their distribution between gas and particle phase. To our best knowledge our measurements constitute the longest time series of amine concentration measurements that have been made.
The measurements covered about 8 weeks from March 2015 to December 2015. With MARGA-MS we were able to separate and detect 7 different amines: monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA), propylamine (PA) and butylamine (BA).

RESULTS AND DISCUSSION

Figure 1 shows the monthly means of total amine concentrations (sum of gas and aerosol phases). The amines were found to be an inhomogeneous group of compounds, showing different seasonal and diurnal variability.

MMA peaked together with the sum of ammonia and ammonium ion already in March, possibly due to evaporation from melting snow and ground. Monthly means in March were $<2.4 \text{ ng m}^{-3}$ and $6.8 \pm 9.1 \text{ ng m}^{-3}$ in gas and aerosol phase, respectively, for MMA and $52 \pm 16 \text{ ng m}^{-3}$ and $425 \pm 371 \text{ ng m}^{-3}$, respectively, for $\text{NH}_3$ and $\text{NH}_4^+$. Monthly medians in March were $<\text{DL}$, 19 ng m$^{-3}$ and 90 ng m$^{-3}$ for both kind of MMA, $\text{NH}_3$ and $\text{NH}_4^+$, respectively.

Figure 1: Monthly mean box and whisker plots of the most abundant amines (sum of gas and particle phases) and summed up ammonia and ammonium. Boxes represent second and third quartiles and vertical lines in the boxes median values. Whiskers show the highest and the lowest observations.
DMA and TMA had summer maxima indicating biogenic sources, but no clear diurnal variation was observed. The highest concentrations of these compounds were measured in July. Monthly means in July were <3.1 ng m\(^{-3}\) and 8.4±3.1 ng m\(^{-3}\) in gas and aerosol phase, respectively, for DMA and 0.4±0.1 ng m\(^{-3}\) and 1.8±0.5 ng m\(^{-3}\) for TMA, monthly medians were <DL and 4.9 ng m\(^{-3}\) in gas and aerosol phase, respectively, for DMA and 0.4 ng m\(^{-3}\) and 1.4 ng m\(^{-3}\) for TMA.

EA concentrations were low throughout the measurements, but showed a clear diurnal variation in July with a maximum at night. Monoterpene concentrations were measured simultaneously at the same site and they correlated well with EA concentrations. This could indicate that EA has a biogenic source.

The results of the linear regression analyses of the amines, and the ambient conditions are presented in Table 1. In the gas phase the p values are especially low for correlations between DMA and any of the ambient condition parameters, suggesting that DMA concentrations increase with increasing air temperature, soil temperature and soil humidity but decrease with increasing atmospheric humidity and wind. The second strongest correlations are those of TMA vs environmental conditions. Interestingly, TMA concentration seems to decrease with increasing air and soil temperature, in contrast with the correlation between DMA and temperature. TMA concentrations were high in spring and they are likely to originate partly from melting snow and ground, whereas DMA might have biogenic sources in summer, which could explain different correlation behaviour.

In addition to the dependency of amine concentrations on ambient conditions, the relationships between particle number and amine concentrations were studied with a similar regression analysis. The amine concentrations were compared with the total number concentration integrated from the size distributions measured with a DMPS (N\(_{100}\)), with the particle number concentrations in the size ranges 1.1-2 nm and 2-3 nm, measured with the PSM (N\(_{1.1-2nm}\) and N\(_{2-3nm}\), respectively) and with the particle number concentrations between 3 and 25 nm measured with the DMPS (N\(_{3-25nm}\)). There was a weak positive correlation between DMA concentrations and the PSM detected cluster-mode particles even though there were only 33 data points and the correlation was statistically not significant (r\(^2\) = 0.06, p = 0.18). The correlation had some dependence on the ambient conditions: air relative humidity (RH) and temperature (t) as well as soil temperature (ST) and soil humidity (SH). The correlation was more significant when both soil and air were humid (RH > 90 %, SH > 0.3 m\(^3\) m\(^{-3}\)) but it has to be noted that there were only 10 simultaneous data points at the high RH. There was no correlation between the slightly larger particles (N\(_{2-3}\)) and DMA in the gas phase, suggesting that DMA took part in the initial steps of particle formation. This is qualitatively in agreement with an experimental CLOUD chamber study where it has been demonstrated that even very small amounts of DMA greatly enhance the formation of nano-particles (Almeida et al., 2013, Lehtipalo et al., 2016). In the aerosol phase DMA was the only amine that had a statistically significant correlation with the cluster-mode particle number concentrations and as for the gas-phase the correlation coefficient was higher at high relative humidity. Other ambient condition parameters apparently did not affect this relationship.
Table 1. Regression statistics \((y = \beta_1 x + \beta_0)\) of amine concentrations in the gas or aerosol phase vs. ambient conditions and aerosol number concentrations. \(r^2\): Pearson's correlation coefficient; s.e.: standard error of \(\beta_1\); d.f.: degrees of freedom; \(t = \beta_1 / \text{s.e.}\); \(p\): p-value of the Student's t distribution; air T: air temperature; RH: relative humidity of air; WS: wind speed at 16.8 m; soil T: soil temperature; soil Hum: soil humidity; \(N_{\text{tot}}\): particle number concentration integrated from the size distributions measured with the DMPS; \(N_{1.2-2\text{nm}}\) and \(N_{2-3\text{nm}}\): particle number concentrations in the size ranges 1.2 – 2 nm and 2 – 3 nm, measured with the PSM; \(N_{3-25\text{nm}}\): particle number concentrations between 3 and 25 nm of the DMPS. The line of DMA(*) was calculated by using only those data that were measured when RH > 90%. Results are shown only for those regressions that have a \(p\) value < 0.1. Very low \(p\)-values are highlighted by bold font.
CONCLUSIONS

The amines turned out to be a heterogeneous group of compounds; different amines are likely to have different sources. All amines had higher concentrations in aerosol phase. MMA and TMA concentrations were highest in spring. Melting of snow and ground can be the source of these compounds. Measured concentrations of summed up ammonia and ammonium were also highest in spring and the share of ammonia increased towards summer.

TMA has an additional maximum simultaneously with DMA during summer, which could indicate biogenic source. However, unlike EA, they did not show similar diurnal variation as monoterpenes. This missing daytime minimum can be due to light dependent biogenic source, or TMA and DMA might be re-emitted from surfaces during daytime, when temperature increases. DMA concentrations had weak positive correlation with cluster-mode particles and correlation had some dependence on the humidity and temperature of soil and air.

ACKNOWLEDGEMENTS

The research was supported by the Academy research fellow project (Academy of Finland, project 275608) and Centre of Excellence (Academy of Finland, grant no. 307331).

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TOWARDS MONITORING OF ICING CONDITIONS WITH OPERATIONAL CEILOMETER NETWORK AND EVALUATION OF ICING FORECAST MODEL

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Keywords: Ceilometer, remote sensing, in-situ observation, icing forecast modelling.

INTRODUCTION

Super-cooled liquid water containing clouds are frequent over Finland. Such clouds have significant potential for causing icing and producing precipitation (including freezing rain). Icing is a challenge, as an example, for aviation and road traffic. Unfortunately, for numerical weather prediction models, occurrence of super-cooled liquid water layer and icing conditions is challenging to forecast. Observations enable evaluation of forecasts of an icing model. Additionally, specific observations could improve near-real-time (NTR) monitoring of icing conditions.

Ground-based remote-sensing instruments enable cloud, aerosol and boundary layer research in high temporal and spatial resolution. Best benefit is evidently gained by multi-sensor synergy (Illingworth et al., 2007). During last decades, several European countries have been able to setup a multi-sensor (including cloud radar, lidar, microwave radiometer) measurement stations for improving quality of cloud research within Cloudnet network. Additionally, there is even much vaster network of single ceilometers (up to several hundreds of sensors in European wide and currently more than ten in Finland) which collect backscatter profiles of aerosol particles and hydrometeors. The ceilometer network has traditionally been used for monitoring cloud ceiling at airports. In this study, we investigate capability of ceilometer backscatter coefficient observations for icing condition monitoring in NRT. In addition, we make first preliminary evaluation of FMI’s icing model forecast skill.

METHODS

Observations utilized in this study include backscatter coefficient profiles of Vaisala CL51 ceilometer and in-situ icing rates measured at two heights (115 m and 272 m) of a tall tower. Observations were made in Vehmasmäki-Kuopio, Finland (Hirsikko et al., 2014) between January 1st and February 16th, 2017. Additionally, evaluated are forecasts of FMI’s icing model. The icing forecast model follows ISO STANDARD 12494 (Makonen, 2000) and has been previously used in production of Finnish Icing Atlas (Hämäläinen and Niemelä, 2017). Input variables of the icing model result from FMI’s operational weather prediction model HARMONIE, which thus, principally determines icing forecast skill.

As a standard ceilometer measurement output includes profiles of attenuated backscatter coefficient. In this work, we have developed a preliminary icing classification scheme (Fig. 1) for hydrometeors observed in backscatter profiles. The method finds liquid water droplet containing clouds from ceilometer data alone by following the Cloudnet scheme (excluding contribution from a cloud radar). Freezing potential of liquid cloud layer is determined based on temperature. Precipitation from a liquid water droplet containing cloud is included into the classification. Type of precipitation is not further classified.
but only divided into warm and cold precipitation. The presented classification scheme is preliminary, and thus, improvements are expected and will be reported elsewhere in due time. Additionally, the measurement period utilized here is relatively short. Therefore, we consider presented results as preliminary.

Figure 1. Preliminary classification for icing potential of liquid droplet containing clouds (dark blue, red, orange and grey colours) and subsequent precipitation (light red and blue colours) in Vehmasmäki-Kuopio on February 12th 2017.

CONCLUSIONS

Before going to operational, every forecast model has to be evaluated. The evaluation is best done with suitable observations. The icing model of FMI is primarily evaluated with in-situ icing rate observations from one or two heights in two location in Vehmasmäki-Kuopio area. Here we report analysis of observations from Vehmasmäki (Tables 1-2). Results suggest that icing conditions occur roughly 40 % of time at both measurement heights. However, model forecasts suggest almost two times higher occurrence of icing. This relatively large difference is expected to arise from forecast skill of liquid water content by HARMONIE model. This particular version of HARMONIE has shown tendency to have too low boundary layer height and cloud base, too much cloud cover, and too much fog in particular over sea (Bengtsson et al., 2017).

FMI has a network of profiling ceilometers, and number of sensors in the network is increasing. In this study, we also investigate potential of a ceilometer to pinpoint icing conditions (Fig. 1). Comparison with in-situ sensor observations indicates that these two sensor types observe icing condition almost as often, simultaneously 64-85 % of time periods when ceilometer had observed icing condition (Tables 1-2). Adding precipitation in classification increases number of simultaneous observations between these two observation scales.
<table>
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Table 1. Comparison between theoretical prediction for icing conditions and experimental detection with ceilometer and in-situ icing sensors. Observations were temporally gridded to half an hour intervals and shown are number of data points when icing condition was observed or forecasted with each sensor or model, respectively, or simultaneously. Observations cover time period between January 1\textsuperscript{st} and February 16\textsuperscript{th} 2017.

<table>
<thead>
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<th>Detection/forecast frequency</th>
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<td>Compared to number of icing conditions observed with ceilometer</td>
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<tr>
<td>In-situ</td>
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<td>In-situ (ceilometer clouds)</td>
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Table 2. Comparison between theoretical prediction for icing conditions and experimental detection with ceilometer and in-situ icing sensor. Values for the Table 2 were calculated based on values reported in the Table 1.
ACKNOWLEDGEMENTS

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WET DEPOSITION SCHEME IN ECHAM-HAMMOZ CLIMATE MODEL

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Keywords: climate modelling, wet deposition.

INTRODUCTION

Atmospheric aerosols affect the climate directly by reflecting and absorbing radiation and indirectly through aerosol-cloud interactions. Thus, in order to estimate the earth’s radiation budget correctly, aerosol concentrations have to be modelled correctly, which is, among others, affected by aerosol transport. Especially with respect to the arctic areas, the transportation of aerosol species is usually underestimated in global models and one of the possible sources of this problem is wet deposition. Here we isolate the wet deposition module of the aerosol-climate model ECHAM-HAMMOZ into a boxmodel setting for future modifications of the module.

METHODS

In this study we use the aerosol-climate model ECHAM-HAMMOZ (ECHAM6.3-HAM2.3-MOZ1.0; hereafter referred to as ECHAM6) which solves the equations for vorticity, divergence, surface pressure and temperature using spherical harmonics with a triangular truncation. The model calculates cloud liquid water and ice and also has a prognostic-statistical scheme to predict cloud cover. ECHAM6 is coupled with the Hamburg Aerosol Model (HAM2.3) which was developed to examine the interactions between climate and aerosols (Stier et al., 2005). HAM models all aerosol processes within ECHAM6, including emissions, deposition, aerosol-radiation interaction and aerosol microphysics (Bergman et al., 2012). ECHAM6 is further coupled with the Model of Ozone and Related Chemical Tracers (MOZ1.0) which is a three dimensional chemical transport model (Horowitz et al., 2003).

ECHAM6 has two different aerosol microphysics packages, M7 and SALSA. M7 is a modal microphysics module, which represents the aerosol distribution using a superposition of seven lognormal modes. The modes included are nucleation, Aitken, accumulation and coarse, which are further divided into a soluble and an insoluble (excluding the nucleation mode) population, amounting to a total of 7 modes (Croft et al., 2009). The Sectional Aerosol module for Large Scale Applications (SALSA) microphysics package uses a moving center sectional approach to describe the aerosol population. The aerosol population is divided into 3 sub-regions. The first sub-region spans sizes from 3 to 50 nm, the second from 50 to 700 nm and the third from 700 nm to 10 µm. Subregions 2 and 3 are further divided into a soluble and an insoluble population. The subregions are divided into logarithmically equi-distant size sections (bins). Subregion 1, 2 and 3 include 3, 4 and 3 size bins, respectively, which amounts to a total of 17 size bins (Kokkola et al., 2008; Bergman et al., 2012).

The wet deposition module in ECHAM6 is divided into two parts: in-cloud and below-cloud scavenging. The in-cloud scavenging scheme has two kinds of scavenging: cloud nucleation scavenging and size-dependent in-cloud impaction scavenging. Cloud nucleation scavenging calculates the scavenging ratios for different sized particles from the cloud droplet number concentration (CDNC) and ice crystal number concentration (ICNC) for liquid, mixed and ice clouds in stratiform clouds. For convective clouds only a mixed cloud phase case is considered, with different scavenging ratios for aerosol size class. For...
stratiform clouds, CDNC and ICNC are prognostic variables. The total number of aerosols that are scavenged is the sum of newly formed CDNC and ICNC in each time-step (Croft et al., 2010).

The below-cloud scavenging scheme has two independent parameterizations for rain and for snow. The parameterization for rain assumes that raindrops, which are acting as the collectors, follow a size distribution, and the scavenging coefficients are a function of both aerosol and collector drop size. The parameterization for snow uses a size-dependent collection efficiency for snow, where the snow crystals are assumed to have a radius of 0.5 mm, a terminal settling velocity of 80 cm/s and a mass of 30 µg (Croft et al., 2009).

In this study the ECHAM6 wet deposition scheme in a boxmodel setting was used, which includes extracting the wet deposition module from ECHAM6, building the supporting modules and operating the ensemble with the same set of parameters used within the climate model. The advantages of a boxmodel are that it takes less calculating time than the whole climate model and easier control of the parameters that affect wet deposition.

The boxmodel needed a driver program, which provides the basic input parameters to the module. These parameters include control parameters, like number of levels, tracer index and in-cloud and below-cloud scheme flags, as well as ambient conditions, like temperature, rain rate, snow rate, etc. The latter set of parameters and the tracer mixing ratios, which serve as input to the module, were sampled from a short ECHAM6 simulation (1 month plus spinup).

Additional supporting modules were needed for physical calculations of log-normal aerosol distributions and critical radii of different aerosol size classes. For each aerosol size class, the model has up to 7 different mixing ratios: total aerosol number as well as mass mixing ratios for sulphate, black carbon, organic carbon, sea salt, mineral dust and aerosol water. For M7, for instance, the entire aerosol distribution is described using a total of 29 tracers. For these tracers, a tracer definition module was implemented, which defines all settings for the individual tracers. Based on the input parameters provided by the driver program, the wet deposition module calculated the wet deposition tendencies for each tracer according to a scavenging fractions from in-cloud and below-cloud schemes (Croft et al. 2009 and 2010), which were then evaluated against the tendencies calculated in ECHAM6.

CONCLUSIONS

Figure 1 shows an example scatterplot of how well the wet deposition tendencies for sulphate aerosols correlate between the full climate model and the boxmodel setting. The data were taken from one gridbox coordinate at all vertical levels over a modelling period of hour, in 7.5 minute intervals.
The boxmodel calculates the tracer tendencies very well compared to the climate model, with only slight fluctuation due to technical limitations. This result makes us confident that the boxmodel setting can be used for further refinement of the wet deposition scheme in ECHAM6.

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REFERENCES


NEW CALIBRATION METHOD FOR THE CONDENSATION PARTICLE COUNTERS

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Keywords: aerosol particles, calibration, number concentration, singly charged, SCAR.

INTRODUCTION

Particles with different charge and size combinations can have the same electrical mobility and cause errors in number concentration and size calibrations. Jaakko Yli-Ojanperä et al. (2010) built a device named single-charged aerosol reference (SCAR) to prevent the error caused by multiply charged particles. The device generates narrow particle size distribution of singly charged particles and can be used to calibrate instruments measuring the number concentration of particles. In this study, a calibration device similar to SCAR was built and its performance was assessed. This device can be used to calibrate condensation particle counters.

METHODS

The built calibration device is presented in figure 1. Primary silver particles are generated in tube furnace and charged bipolarly with $^{14}$C --charger. Differential mobility analyser (DMA) selects 10 nm-sized particles, which are led to the second tube furnace. Diethylhexyl sebacate (DEHS) inside the furnace evaporates and condensates onto particles and they grow to larger sizes. The second DMA selects given size from the grown particles. The TSI 3772 -condensation particle counter and reference TSI 3068 B - electrometer measure particle number concentration from the output of the device. Particle size distribution can be adjusted by changing the temperature of the second furnace or DMA flow rates. Smaller particles 10 – 100 nm were measured with Short Hauke DMA operated with 20/2 lpm flow rates and larger particles 100 – 1000 nm were measured with long Hauke DMA operated with 5/2 lpm flow rates.

Figure 1. Parts of the calibration device.
CONCLUSIONS

Figure 2 shows primary size distribution, the distribution through the DMA and charging probabilities for negative charges 1 and 2 calculated from Wiedensohler’s equation (Wiedensohler, 1988). The distribution through the DMA is very narrow with geometric standard deviation of 1.1 compared to the primary size distribution with standard deviation of 1.3. Fraction of the doubly charged particles in the distribution through the DMA was calculated from the primary size distribution and it was only 0.043%. Therefore, the particles passing through the DMA have 99.96% singly charged particles. When these particles grow through condensation, they should remain singly charged and generate monodisperse size distribution. Singly charged particles were generated in the size range of 12 – 1000 nm with standard deviations of 1.1 – 1.2. The built calibration device worked almost as well as SCAR but it did not reach higher concentrations than 20 000 cm$^{-3}$.

![Figure 2. Distributions and charging probabilities of negative elementary charges 1 and 2.](image)

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REFERENCES


A WHOLE TREE LEVEL MODEL OF STOMATAL CONDUCTANCE MAXIMIZING TREE METABOLIC RATE

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Keywords: PHLOEM TRANSPORT, STOMATAL CONTROL, SINK LIMITATION, XYLEM TRANSPORT

INTRODUCTION

Water and carbon exchange occur in opposing directions in a tightly controlled manner at the vegetation-atmosphere interphase through stomatal openings in the leaves of vascular plants. The loss of water from the leaves to the atmosphere is replaced with water flow from soil through the xylem, while part of the xylem sap flow is needed for turgor driven transport of the assimilated carbohydrates in the phloem from leaves to sites of consumption in sugar sinks. We demonstrate using a numerical model that stomatal functioning can be understood from the viewpoint of maximizing the simultaneous photosynthetic production, phloem transport, and sink sugar utilization rate (Hölttä et al. 2017).

METHODS

Equations describing source, transport and sink processes were solved so that the plant metabolic rate was maximized (Fig. 1). A key feature in our model is that non-stomatal limitations to photosynthesis increase with increasing leaf sugar concentration and are thus coupled to stomatal conductance.

Figure 1. Equations describing source, sink and transport processes with a tree.
RESULTS

Maximizing the photosynthetic production rate using a numerical steady-state model leads to stomatal behaviour that is able to reproduce the well-known trends of stomatal behaviour in response to e.g. light, VPD, ambient CO2 concentration, soil water status, sink strength, and xylem and phloem hydraulic conductance (Hölttä et al. 2017). Predictions for stomatal conductance are also very similar to the predictions given by the “unified stomatal control model” (e.g. Medlyn et al. 2011) and the “optimal stomatal conductance model” (e.g. Hari and Mäkelä 2003). Our modeling results also demonstrate how the “marginal cost of water” in the unified stomatal conductance model and the optimal stomatal model could be related to plant structural and physiological traits, most importantly, the soil-to-leaf hydraulic conductance and soil moisture (Hölttä et al. 2017).

DISCUSSION AND CONCLUSIONS

Carbon assimilating leaves and carbon sinks are connected to each other through xylem and phloem so a key task of stomatal regulation is to match leaf gas exchange to the internal circulation of sap in trees. When water potential or sugar concentration of one tissue within a tree changes, xylem and phloem propagate this change to other tissues (Nikinmaa et al. 2013). Since the rate of both source and sink processes are dependent on local water and carbohydrate status, any changes in sink status will be reflected to source status and vice versa. Our numerical analysis utilizing this theoretical framework demonstrates that the previously well-known responses of stomatal behaviour are in good agreement with maximizing the photosynthesis rate in steady state when the above source-sink connection and tree hydraulics are considered.

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REFERENCES


COMPARING STATISTICAL DIMENSION REDUCTION TECHNIQUES IN THE ANALYSIS OF MULTIVARIATE ATMOSPHERIC DATA

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Keywords: dimension reduction, pmf, pca, multivariate time series

INTRODUCTION

Online mass spectrometry monitoring techniques applied in atmospheric studies produce complex datasets with a large number of long time series. Statistical dimension reduction techniques are developed to compress the information from a large number of correlated variables to a small number of latent variables, which can be interpreted according to their physical or chemical properties. In atmospheric research, Positive Matrix Factorization (PMF), developed in mid-90s by Paatero and Tapper (1994), is currently the most exploited method for the analysis of long time series of Aerosol Mass Spectrometer (AMS) and Chemical Ionisation Mass Spectrometry (CIMS) data. PMF was developed because mass spectrometry data contains concentrations of the investigated compounds and are therefore constricted to positive values. PMF answers that need adequately because the factorization matrices created are also constricted to positive values, which simplifies the interpretation of the results.

Factorization methods, including Principal Component Analysis (PCA) and Exploratory Factor Analysis (EFA, hereafter only Factor Analysis, FA), are widely utilized in many different fields of science, e.g. in psychological and medical studies, when multivariate data is investigated (Fabrigar et al., 1999; Raskin et al, 1988). However, recently also Wyche et al. (2015) used PCA in the analysis of the large datasets produced in their smog chamber measurements and gained promising results.

METHODS

For preliminary studies, we applied Principal Component Analysis, Factor Analysis, Positive Matrix Factorization and Non-negative Matrix Factorization to the same dataset. In principle, all these methods are solving the bilinear matrix equation

\[ X \approx WH, \] (1)

Where \( X \) is the original data matrix and \( W \) and \( H \) are the resulting factorization matrices. PCA and FA, solve the problem using correlation or a covariance matrix formed by the original variables in \( X \) whereas PMF and NMF create the approximation \( WH \) from data matrix directly.

PMF is a special case of NMF and we used PMF2-application (Paatero, 2007) in our calculations. For NMF, we used the brunet-algorithm introduced in Brunet et al. (2004). Factorization matrices acquired when solving equation (1) can be rotated for better interpretation. We used orthogonal varimax-rotation for the factors in FA. In order to compare these methods in a meaningful way, the factor variables needs to be scaled to the same magnitude, as PMF and NMF constrain the factor variables.
RESULTS

Figure 1 illustrates the different outcome from different factor analysis methods. The data for the comparison was collected during a plant emission measurement campaign in 2015, where Scots pine saplings were exposed to bark feeding pine weevils. The emissions were monitored continuously by Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS).

Three factors were identified from the plant emission data: background, diurnal cycle and plant stress. Factors were most interpretable when using FA yet all of the methods used were able to construct identifiable plant stress factor; rising when the feeding period starts and decreasing when the weevils are removed. PCA combines the diurnal cycle and plant stress factors, most probably because the diurnal cycle is rising during the active feeding period as well. PMF and NMF created two factors, which both seem to be involving the diurnal cycle and were not able to distinct the background from those. Factors acquired from PMF and NMF got negative values after scaling. Results from PMF, NMF and PCA would possibly improve if we would add more factors/components to the analysis.

Figure 1. Factor/component scores created from Scots pine emissions. Shaded area indicates the active feeding period of the pine weevils.
One of the problems when comparing the outcomes from different factor analysis methods is related to the calculation method utilized when constructing factor matrices. PMF and NMF are solving the bilinear matrix problem (Eq. 1) directly, but the calculation in PCA and FA are based on the correlation matrix between the measured variables. One of the aims in our study is to find quantitative measure to compare the results acquired from these methods. In order to compare these methods appropriately, we will create artificial data by handpicking the variables from the real physical emission data, which has already been studied thoroughly. The benefit of this approach is that the outcome of the analysis is well known beforehand. In addition, measurement data from different campaigns and from different monitoring techniques including e.g. Time-of-Flight Chemical Ionization Mass Spectrometry (ToF-CIMS) will be used to test the mathematical efficiency of each of these methods.

CONCLUSIONS

There have been some comparisons between PCA and FA for certain types of data (e.g. Suhr et al., 2005). Comparisons between PMF and PCA have also been made, most of them by Paatero when he introduced PMF to overcome the interpretation-related problems of the results from PCA. However, thorough comparisons between multiple factor analysis methods are missing. We intend to test other statistical dimension reduction techniques as well (not presented here) and create references or guidelines for the methods; which fits best for what kind of data or should at least be tested during the analysis.

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REFERENCES


INTRODUCTION

Approximately 338 million people live in snow-covered regions in the Northern Hemisphere but there is still little knowledge on the local hydro-climatology of the cities that are affected by snow. The most dramatic climate change is expected at high-latitudes (Xia et al., 2014) and therefore it is particularly important to understand how climate variations will potentially affect the surface energy and water balances and local climate in urban areas in these regions. Already now significant decreases in high latitude snow cover duration and spatial extent have been observed (Stone et al., 2002; ?), which has been found to result in induced peak flows and more runoff throughout winter. Snow controls urban surface properties via changes in albedo, thermal insolation and water availability, thus its effects on the urban climate hydrological cycle are of principal importance. The purpose of this study was assess and understand the combined impact of climate and urbanisation on the urban hydrological cycle in cold climate regions where snow in winter is commonly observed.

METHODS

The model used in the study to simulate the hydrological cycle was the Surface Urban Energy and Water balance Scheme (SUEWS, Järvi et al 2011). The model was run at 11 sites in four cities in Europe and North America (Helsinki, Finland; Basel, Switzerland; Montreal, Canada; and Minneapolis-Saint Paul, USA). The areas vary with respect to land cover fractions, population densities and human activities. For example, the plan area fraction of impervious surfaces varies from 5% in Minneapolis to 84% in Basel. As the modeled time periods are for one (Basel) to 7.5 years (Helsinki), a wide range of meteorological conditions occur. For each site, the model is run in an offline mode using measured hourly meteorological data with a time step of 5-min.
CONCLUSIONS

Our results show how in snow critically changes the impact of the city design on the local-scale hydro-climatology (Järvi et al., 2017). In winter the presence of snow obliterates the influence of the surface cover characteristics and the cities return to being strongly controlled by the built-vegetation partitioning only after snow melt. Inter-year variability of wintertime temperature further modifies the effect. With increasing temperatures these cities are pushed towards very different partitioning between runoff and evapotranspiration, and sensible heat and latent heat flux. We derive the dependency of wintertime runoff on this warming effect in combination with the effect of urban densification.

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REFERENCES


THE EFFECTS OF ELEVATED GROUND SURFACE OZONE ON THE GROWTH AND PHYSIOLOGY OF JAPANESE LARCH AND ITS HYBRID SEEDLINGS

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INTRODUCTION

The ground surface ozone (O₃), a phototoxic air pollutant to inhibit physiological activities of plants, has increased in the northern hemisphere over the past three decades and it is still increasing. Atmospheric environment condition in northeast Asia has deteriorated due to the rapid economic development. Relatively high O₃ (over 100 ppb) has been frequently detected in central Japan. In addition, nitrogen (N) deposition has also increased by the industrial development and economic growth although N is an essential element for plant growth. However, excessive N deposition as much as 50 kgN ha⁻¹ year⁻¹ may influence the imbalanced development of each organ in plant.

Larch species are widely distributed in northern Japan as well as eastern Eurasia. In this context, larch species is one of key species in ecological and global points. Japanese larch (Larix kaempferi; JL) was introduced from the central part of Japan to the northern part. The JL has fast growing traits with resistance to low temperature and nutrient. However, it is susceptible to shoot blight disease and grazing by voles. To improve the demerits of JL, hybrid larch F₁ (HL) was developed by crossing Larix gmelinii var. japonica and JL, and it has greater capacity for carbon accumulation than JL.

METHOD

1) The effect of increasing O₃ concentration on JL and HL

Two year-old seedlings of JL and HL were planted in brown forest soil in June, 2013. For the different O₃ level treatment, open-top chamber systems were established on the study site (Sapporo experimental forest of Hokkaido University). The seedlings of JL and HL were exposed to four different O₃ concentrations: charcoal filtered air (< 5 ppb) and three levels of non-filtered air with O₃ (< 25, 40 and 80 ppb) during daytime.

2) The interactive effect of elevated O₃ and N deposition on JL and HL

The 2 year-old JL and HL seedlings were planted in 15 L pots filled with the simulated immature volcanic ash soil in June 2013. For O₃ treatment, a free-air O₃ fumigation system (Dalton Ltd, Sapporo, Japan) was established, and seedlings were grown under 60 ppb ozone concentration. In order to simulate acid rain of the current condition in Japan, NH₄NO₃ (47 kg N ha⁻¹ year⁻¹) solution applied to the potted soil.

CONCLUSION

In order to investigate the effect of increasing O₃ concentration between JL and HL, the 2-year-old seedlings of JL and HL were grown under increasing O₃ concentration from 5 ppb to 80 ppb with open top chambers. The whole-dry mass of JL and HL was decreased by O₃ concentration, and the increasing O₃ concentration inhibited photosynthetic activities of seedlings, which induced the suppressed root growth.
development of HL at 80 ppb and reduced T/R ratio. The impaired stomata conductance of HL at 80 ppb may result in the highest amount of ascorbic acid content for the antioxidant scheme. Ascorbic acid (an anti-oxidant) concentration of HL was the highest in 80 ppb.

N supplied to soil would change the O$_3$ susceptibility of JL seedlings. Excessive N deposition would impair the soil condition, which may induce the nutrient imbalance in plants. Hence, under elevated O$_3$ concentrations, interactive effect of adequate and excessive N deposition with O$_3$ is important for an improvement of larch plantation. The growth of HL was inhibited by excessive N treatment. The N re-translocation rate from needles to plant body of JL and HL was suppressed by elevated O$_3$. 
A NEW “1 NM” HIGH FLOW DMPS BASED ON HALF-MINI DMA AND A11, AND SUB-10 NM PARTICLE OBSERVATIONS IN BOREAL FOREST IN HYTTYÄLÄ, FINLAND

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Keywords: DMPS, SUB-10 NM, PARTICLE

INTRODUCTION

A differential mobility particle sizer (DMPS) is the most commonly used instrument to obtain particle size distributions. A traditional DMPS system consists of a sampling line, aerosol charger, differential mobility analyzer (DMA) and a condensation particle counter (CPC) (Wiedensohler et al. 2012). By characterizing the particle losses in the sampling line, charging probabilities in the charger, penetration in the DMA and detection efficiency of the CPC, one can back calculate the particle concentration at the DMPS inlet from the particle concentration detected by the CPC. Often, especially in the sub-10 nm particle concentration measurements, the number of particles, N, detected by the CPC can be low due to particle losses in the sampling line and low charging probabilities, leading to uncertainties in the inverted concentration. This is because particle sampling is a random Poisson process, in which the relative counting uncertainty can be estimated as $\sqrt{N/N}$ (Kangasluoma and Kontkanen 2017). Further, inaccuracies in the inversion can originate from the characterization (or lack of it) of the sampling lines, charging probability and DMA transmission. All these accumulate to the particle concentrations measured by the DMPS systems, making the sub-10 nm particle concentrations especially inaccurate (Wiedensohler et al. 2012).

In this study we characterize a DMPS system based on SEADM Half-mini type DMA (Fernández de la Mora and Kozlowski 2013), here after high flow DMPS (HFDMPS). Our goal is to optimize the DMPS technology in every aspect for sub-10 nm particle measurements, meaning minimized and characterized particle losses in each part of the system as well as improved detector in terms of counting statistics as compared to the existing systems. We characterize the HFDMPS system for particle penetration in the sampling line, charger, DMA and for the detection efficiency of the detector, the Airmodus A11. The data obtained from the HFDMPS will be compared to the long term DMPS and A11 systems operated in Hyytiälä.

EXPERIMENTAL

We start the characterization experiments by measuring the particle size dependent transmission of the core sampling line, $^{14}$C charger and DMA. The test particles were generated with a glowing wire generator and size classified with a Herrmann type DMA. The sampling line used in atmospheric experiments was characterized so that two TSI 3068B electrometers were placed upstream and downstream of the sampling line, and size dependent particle penetration, $P_{\text{line}}$, was measured between 1 and 5 nm. The penetration of the $^{14}$C charger, $P_{\text{charger}}$, was measured as previously, but due to the ions generated, we used the A11 as the detector downstream of the charger at supersaturation low enough to not detect any ions. In similar fashion, we measured the Half-mini DMA transfer function surface area, $\Omega_{\text{DMA}}$, by guiding a known concentration of size selected ions between 1 and 5 nm to the DMA, and measuring the integral of the concentration downstream of the DMA. The DMA resolution was measured by generating positively charged tetraheptylammonium (THA$^+$, $C_{28}H_{60}N^+$) ion (Ude and Fernández de la Mora 2005) with the Herrmann DMA, and scanning the corresponding voltage range with the Half-mini DMA. For the A11 detection efficiency, $D_{\text{A11}}$, calibration we used two different test particles to probe the composition
dependent particle activation by diethylene glycol (DEG) (Jiang et al. 2011; Kangasuoma et al. 2014; Kangasuoma et al. 2016). The particles were generated either with the wire generator as described above to measure chromium trioxide particles, or with the electrospray source by producing negatively charged tetraheptylammonium bromide clusters (Ude and Fernández de la Mora 2005). As described above, we characterized the whole HFDMPS piece by piece. When taking the product of all penetrations, one obtains the total penetration of the system (excluding the charging probability which was not verified):

\[ P(D_p) = P_{\text{line}}(D_p) \times P_{\text{charger}}(D_p) \times \int_0^\infty \Omega_{\text{DMA}}(D_p) \times P_{A11}(D_p) \]

It is possible that one obtains different \( P \) when using the system as one unit due to some experimental artefacts or unknown line penetration in the lines connecting the different pieces. Therefore we conducted a full system calibration so that particles of 2 – 10 nm were guided to the whole HFDMPS system, and the detected signal was compared to a reference electrometer.

For atmospheric measurements the HFDMPS was taken to Hyytiälä, Finland, SMEARII measurement station. The HFDMPS was sampling atmospheric air 22.4-18.5 during the spring of 2017.

RESULTS

Figure 1 presents the \( P \) of the HFDMPS as a function of particle diameter for each part of the system, and the whole system measured separately. \( P_{A11} \) is approximated from the curve measured with negatively charged \( \text{CrO}_3 \) to be constant of about 0.60, which takes into account the A11 internal losses, about factor 0.85, and sample flow dilution in the A10, factor of 2.5/(1+2.5) = 0.71. Additional factor of 0.8 was found in the whole system measurements, which is due to particle losses in the flow split downstream of the DMA, which is to increase the DMA aerosol flow rate to total of 5 lpm. The two separately measured \( P \)s agree within ±5% accuracy with each other. Most probably the largest uncertainties in \( P \) accuracy are related to the particle charging probability, which we are unable to speculate here.

From atmospheric data we compile all data from the campaign into single plots, which are presented in Figure 2. The particle concentration measured by the HFDMPS in size range 3 – 1000 nm was calculated so that concentration between 3 and 10 nm was taken from the HFDMPS, 10 and 1000 nm from the DMPS, and those were summed up. The A11 concentration is the raw concentration measured by the A11
at its highest $d_{50}$ (saturator flow rates smaller than 0.11 lpm), which, due to lack of exact knowledge, was estimated to be 2.5 nm. We assume that the A11 detects all particles above this 2.5 nm threshold. Panel A shows the concentration ratio between a DMPS system and the A11 for bihourly averages. The median values for the concentration ratios are 0.93 and 0.79 for the HFDMPS and DMPS, respectively. Thus, presuming the DMPS system measures accurately in the super-10 nm size range, the HFDMPS is still missing about 7% of the particles. There are at least two possible explanations for this discrepancy for the HFDMPS: the A11 $d_{50}$ is lower than 3 nm which is the lowest channel used in the HFDMPS, which allows the A11 to detect more particles, and/or the charging probabilities are overestimated leading to too low inverted concentrations. For the DMPS, added to the previous two, it is possible that the sampling losses are underestimated, as already suggested by Figure 6. Panel B shows all data from the campaign as compared to the A11, exhibiting sound agreement with different concentrations in spite of the offset. Panel C presents the ratio of 3–10 nm particle concentrations from the HFDMPS to the DMPS. We find on median a factor of 2.91 between the two instruments. Since we have used the same charging method and charging probability parametrizations, the discrepancy is most possibly due to the wrongly corrected sampling losses in the DMPS system, as we find closer agreement for the HFDMPS than for the DMPS to our total concentrations reference A11. Panel D shows non-averaged data from the panel C, exhibiting large scatter at low concentrations.

Figure 2. Comparison between the HFDMPS, DMPS and A11 for the one month time period.

CONCLUSIONS

We have built and characterized a new Half-mini DMA based high flow DMPS system, and operated it in Hyytiälä during the spring of 2017. The obtained one month data was compared to the long term DMPS and A11 systems. We found that the HFDMPS cannot be used in Hyytiälä for sub-3 nm particle concentration measurements, for it does not detect such small particles due to the inability of DEG to activate sub-3 nm particles, or lack of charging efficiency (not shown). Thus we analysed the particle concentrations in the size range of 3 and 10 nm against the long term DMPS and A11, and found that concentrations measured by the HFDMPS in this size range are almost by a factor of 3 larger than what the DMPS measures. We believe this is due to incorrect sampling corrections in the DMPS system, as we find better agreement between the HFDMPS and A11, than between the DMPS and A11. However, the HFDMPS measures only 93% of the particles from what the A11 shows in the size range of 3–1000 nm. This can be possibly due to wrong charging probabilities used in the inversion, or lower smallest detectable size of the A11 as compared to the HFDMPS. However, based on this study, we cannot given an estimate on the magnitudes of these discrepancies.
Our observations have few implications on sub-10 nm particle concentration measurements:

1) Sampling plays a crucial role due to high diffusion losses. The sampling lines should be always experimentally characterized.
2) DMPS systems operated with DEG based CPC cannot be used for sub-2(-3) nm particle concentration measurements in systems where those particles are organic species.
3) The higher the number of counted particles, the less counting uncertainties. This calls for high flow CPCs especially if the DMPS system is used in low particle concentration environments.
4) The largest sources of inaccuracy are the lowest detectable particle size and charging probabilities.
5) Sub-10 nm particle concentrations are possibly underestimated in Hyytiälä on average by a factor of 3 in the past measurements.

Related future work will be to begin long term measurements with the current HFDMPS, to calculate particle growth and nucleation rates for a longer time period, and compare them to the past obtained values. Further, the reason for the observed discrepancy of 7% between the HFDMPS and A11 should be cleared.

ACKNOWLEDGEMENTS

We are indebted to the Hyytiälä station staff, J. Levula, S. Rantanen and M. Loponen, for taking care of the HFDMPS during the campaign. This work was partly funded by Maj and Tor Nessling foundation (grant 201700296) and Academy of Finland (Center of Excellence Program projects 307331).

REFERENCES


THE EFFECT OF GASOLINE CAR EXHAUST ON PHOTOCHEMISTRY OF ALPHA-PINENE

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Keywords: α-PINENE, CAR EXHAUST, FACTOR ANALYSIS.

INTRODUCTION

Volatile organic compounds (VOCs) can end up to the atmosphere from two different sources, biogenic or anthropogenic. Annual biogenic volatile organic compound emissions are estimated to be 825-1150 TgC yr⁻¹ (Fehsenfeld et al., 1992; Guenther et al., 1995). Anthropogenic VOC emissions account for ~140 TgC yr⁻¹ (Goldstein and Galbally, 2007). However, in urban areas anthropogenic emissions can dominate VOCs (Warneke et al., 2007; Apel et al., 2010; Parrish et al., 2009). Due to the presence of biogenic and anthropogenic emissions in many locations at the same time, potential interactions between the compounds emitted from these two sources has raised particular scientific interest. There has been different approaches to study these interactions. For example, in order to clarify anthropogenic-biogenic interactions field studies have been conducted in environments where the emissions from these two sources are mixed (Shilling et al., 2013, Hao et al., 2015). Moreover, specific reactions between anthropogenic and biogenic emissions have been studied using environmental chambers and mixtures of pure model compounds typical for specific anthropogenic or biogenic source (Emanuelsson et al., 2013). So far only one controlled laboratory study with a real anthropogenic emission source has been conducted to clarify these interactions (Kari et al., 2017). The laboratory studies with real anthropogenic emission sources represent better the complexity of these interactions than the studies with only pure standards, but still allowing controlled conditions to investigate the processes in systematic way. In this work, we conducted an environmental chamber study to explore possible anthropogenic-biogenic interactions between a gasoline car exhaust and α-pinene; the interactions that are possibly taking place in monoterpane dominated areas with urban influence.

METHODS

As an anthropogenic emission source we used a modern passenger car with gasoline engine (VW Golf 1.2 TSI). The diluted exhaust was fed into the 29 m³ environmental chamber. During the feeding, the car was driven at a constant speed 80 km/h using a dynamometer. The speed of 80 km/h was chosen to represent a normal driving speed in Finland. In this study, we conducted three kinds of experiments under atmospherically relevant conditions to explore the effect of gasoline car exhaust on the photochemistry of α-pinene: 1) experiments with only gasoline car exhaust, 2) experiments with α-pinene and gasoline car exhaust, 3) experiments with α-pinene and ammonium sulphate (AS). Case 3) represents reference experiments to clarify the photochemistry of α-pinene in the absence of gasoline car exhaust. In case 3) the VOC-to-NOx ratio was adjusted so that it was comparable to cases 1) and 2). In these experiments the photochemistry was initiated with UV-lamps (blacklight lamps centered at 340 nm), and H₂O₂ was used as OH precursor.

The VOCs were monitored continuously by proton-transfer-reaction time-of-flight mass spectrometer (PTR-MS, Ionicon Analytik, Austria) and time-of-flight chemical ionization mass spectrometer (ToF-
CIMS, Aerodyne Research Inc., USA) with acetate ionization. The aerosol composition was characterized by aerosol mass spectrometer (SP-AMS, Aerodyne Research Inc., USA). The particle size distribution in the environmental chamber was monitored with a scanning mobility particle sizer (SMPS; TSI 3081 DMA + 3775 CPC). Also O₃ and NOₓ concentrations were monitored using a trace-level chemiluminescence NO-NO₂-NOₓ analyser (Thermo 42i-TL) and an UV photometric ozone analyzer (Thermo 49i).

CONCLUSIONS

Preliminary results are presented in Table 1. As shown in Table 1, there was secondary organic aerosol (SOA) formation from pure gasoline car exhaust. When the formed SOA mass from case 2 (gasoline car exhaust + α-pinene) is compared to SOA mass formed from case 3 (AS + α-pinene), it can be concluded that the car exhaust did not have a significant effect on the formed SOA mass in case 2. Moreover, Table 1 shows that the SOA from car emissions had clearly higher O:C than SOA from α-pinene. It can also be seen from Table 1 that gasoline car exhaust produced different amount of SOA in different experiments. This variation in formed SOA mass is due to the changes in emission composition even if the driving conditions in each experiments were similar. This highlights the complex nature of the studies utilising realistic emission sources.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>α-pinene consumed (ppb)</th>
<th>Formed SOA (µg m⁻³)</th>
<th>O:C ratio at the end of an experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Car exhaust</td>
<td>-</td>
<td>1.4</td>
<td>1.38</td>
</tr>
<tr>
<td>Car exhaust</td>
<td>-</td>
<td>3.7</td>
<td>1.25</td>
</tr>
<tr>
<td>Car exhaust + α-pin</td>
<td>24.5</td>
<td>54</td>
<td>0.78</td>
</tr>
<tr>
<td>Car exhaust + α-pin</td>
<td>4.4</td>
<td>5.5</td>
<td>0.88</td>
</tr>
<tr>
<td>AS + α-pin</td>
<td>24.2</td>
<td>53</td>
<td>0.66</td>
</tr>
<tr>
<td>AS + α-pin</td>
<td>4.8</td>
<td>7.0</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 1. Preliminary particle phase results.

Gasoline car exhaust that was introduced into the environmental chamber contained a complex and varying mixture of different VOCs and particles. Due to the complex and varying VOC composition of exhaust that was further mixed with α-pinene, we applied factor analysis for PTR-MS and ToF-CIMS datasets, in order to find out evidences from the interactions between the gasoline car exhaust and α-pinene. The preliminary results from factor analysis suggests that there are possible interactions between gasoline car exhaust and α-pinene. Data-analysis of this study is in progress and next we will explore with different statistical methods if gasoline car exhaust has any effect on SOA formation from α-pinene.

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REFERENCES


10th YEAR OF CLOUD CONDENSATION NUCLEI MEASUREMENTS AT SMEARII

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Keywords: Atmospheric aerosols, long-term measurements, cloud condensation nuclei, hygroscopicity

INTRODUCTION

The atmospheric aerosols ability act as a cloud condensation nuclei (i.e. hygroscopic properties) has direct consequences about their role in climate change. Here, we have now the 10th year of the particles continuous hygroscopic properties measurements by Cloud Condensation Nuclei counter (CCNc) ongoing at SMEAR II. SMEARII is a 20-year-old research station in Scots pine stand for studying the atmosphere and forest/lake/wetland ecosystem interactions. Currently, the freshly nucleated atmospheric aerosols from nanometer to micrometer scale have been well analyzed based on their e.g. their mass, size and number which has given extremely valuable information of atmospheric aerosol processes like particle formation and subsequent growth (Aalto et al., 2001, Kulmala et al., 2007, 2012, 2013, Petäjä, 2013). We are aware that these nanoparticles in the atmosphere can grow into the size range where they are large enough to act as cloud condensation nuclei (Merikanto et al. 2009). Thus, the long term well-defined, strictly monitored and carefully analyzed CCNc measurements in our station as well around the world (Schemale et al., 2017) are needed to estimate the atmospheric nanoparticles effect on the cloud formation. These well-defined long-term measurements are mandatory when we define the aerosol properties to the large scale climate models. Here, the goal is introduce shortly our current CCNc measurement set-up, what we measure, how we measure, how we qualify the data and where it has and will be used for.

METHODS

The CCNc measurements are performed at SMEAR II (Station for Measuring Earth surface-Atmosphere Relations II) station located in Hyytiälä, Southern Finland (61°51'N, 24°17'E, 181 a.s.l, Hari and Kulmala 2005). The station is equipped with extensive facilities to measure continuously and comprehensively earth surface-atmosphere interactions (Kulmala et al., 2014). Hyytiälä is a rural and background site with low local particle matter emissions. CCNc measurements are located to the Hitu-hut and the sampling lines are located in forest 8 m from ground level (Figure 1a).

Here, the CCNc (Droplet Measurements Technologies) measurements are done in polydisperse and monodisperse measurement mode. In Figure 1b, the photo of our measurement system is shown. First, the sampled atmospheric aerosol is drawn via sampling line into nafion dryer to sustain its humidity low before the actual measurements. Firstly, when aerosol is measured in monodisperse measurement mode it is directly drawn to the CCNc to measure the activated particles and CPC (TSI, model 3770) to measure the total particle counts. Secondly, in the monodisperse mode, the particle size is first selected by the DMA (Wiennese) and the measured by CCNc and CPC. The selected supersaturations in CCNc are 0.1, 0.2, 0.3, 0.5, and 1. The selected mobility diameters (Dm) for the monodisperse measurements are 300, 273.25, 248.89, 226.70, 206.49, 188.08, 171.31, 156.04, 142.13, 129.46, 117.92, 107.40, 97.83, 89.11, 81.16, 73.93, 67.34, 61.33, 55.86, 50.88, 46.35, 42.22, 38.45, 35.02, 31.90, 29.06, 26.47 24.11, 21.96, 20.00 nm. Thus, we can get the critical supersaturation defined by an activation ratio versus SS or Dm. The SS measurements are selected to be same in different measurement stations. Thus, the monitoring of the CCNc activity in worldwide networks such as ACTRIS is possible. The size dependent activity scans have an importance also when we study these nanoparticles chemical composition (Paramonov, 2015).
very accurate size-selected measurements we can achieve important information e.g. particles composition changes vs. the size. However, in accuracy in size we lose accuracy in time. One challenge has been also develop the matlab-codes to process these measurements data-sets to the well qualified data submitted to the networks such as e-bas. To maintain good quality of the measurements we had measured the Ammonium sulfate nanoparticles CCNc activity in every 4th month (Figure 1c). Our system is qualified by World Calibration Centre of Aerosol Physics at years 2009 and 2016.

![Image](image.png)

Figure 1 a) Hitu-hut, b) CCNc measurement unit and c) illustration of the calibration system of the measurements.

**CONCLUSIONS**

We present here our current CCNc measurement unit at SMEARII. These measurements anniversary is at this year as they had been ran from the year 2007. We have here an excellent base for the dataset of the polydisperse and monodisperse measurements in long run. There is still many challenges and research questions ongoing on measurements development and data interpretation for long run. However, these measurements have had already important role when we have estimated the atmospheric nanoparticles CCN impacts in topical in worldwide networks such as EUCAARI (Paramonov et al. 2015) and ACTRIS (Schmale et al., 2017). In the Paramonov study there was found differences in cloud condensation Nuclei number in same supersaturation at certain locations e.g. marine aerosol had higher numbers compared to the remote sites. In that study the hygroscopic properties were resulted to be size depended as expected. However, measurement location had also effect on their size dependency behavior. The latest study by Schmale et al. 2017 the dataset of 11 observatories, spanning 98,677 instrument hours for CCN data, 157,880 for particle, number size distributions, and 70,817 for chemical composition data were summarized from years. This well-defined high quality dataset was published to be utilized for the further studies considering e.g. the detailed aerosol properties understanding and evaluation the model’s representation of the aerosol properties among different measurement environments.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


INTRODUCTION

The breaking of ocean waves by wind creates bubbles, which then burst and release aerosols to the air. The created sea spray aerosol (SSA) contains sea salt and a mixture of organic matter. The ratio of organic matter to sea salt varies according to wind speed and the chemical and biological composition of sea water. The organic SSA can act as cloud condensation nuclei and can have a significant impact on climate. Further details on organic SSA can be found in the review by Gantt and Meskhidze (2013).

Several different approaches that allow the inclusion of organic SSA in climate models have been proposed. Many of these parametrisations use the chlorophyll \(a\) concentrations as a proxy in the calculation for the organic fraction in the SSA (Vignati et al., 2010; Rinaldi et al., 2013; Gantt et al., 2011). In a similar manner, although explicitly involving physical surface chemistry in the calculation of the organic fraction, five different classes of macromolecules are used in the approach by Burrows et al. (2014). The organic fraction can be calculated also using salinity and sea surface temperature (Kasparian et al., 2017).

The present work considers the addition of organic SSA emissions to the global chemistry transport model TM5 and the assessment of its impact on the global aerosol distribution. Two organic SSA parametrisations, one by Vignati et al. (2010) and another by Burrows et al. (2014), were implemented. Our results indicate that the largest impacts of organic SSA can be seen on the Southern Ocean.

METHODS

We studied the organic SSA using TM5 (Huijnen et al., 2010), a global three-dimensional atmospheric chemistry transport model. It has 27 chemical species that are transported according to the meteorological fields from the ECMWF operational forecast data and 15 short-lived chemical species that are not transported. Emissions in the TM5 come from a variety of anthropogenic, biogenic, and biomass burning sources. In its standard form, TM5 does not include any organic SSA emissions.

The aerosol processes in TM5 are handled using the M7 aerosol model (Vignati et al., 2004). It represents particles using seven lognormal modes so that four modes are used to describe the soluble particles and three the insoluble particles. The insoluble modes are the Aitken, the accumulation,
and the coarse modes while the soluble modes include an additional nucleation mode. Seven different aerosol chemical components are considered in the M7: sulfate, black carbon, primary organic carbon, sea salt, and dust.

In order to allow TM5 to be used in studies involving organic SSA, we implemented the parametrisations of Vignati et al. (2010) and Burrows et al. (2014) in TM5. The parametrisation by Vignati et al. (2010) uses the sea surface concentrations of chlorophyll $a$ as a proxy for organic content in the sea spray. The organic fraction $F$ in the accumulation mode SSA depends linearly on the chlorophyll $a$ concentration $C$ so that

$$ F = \begin{cases} 0.435C + 0.13805, & \text{when } C < 1.43 \\ 0.76, & \text{when } C \geq 1.43, \end{cases} $$

where $C$ is given in the units of mg/m$^3$. In the coarse mode, we emit organic aerosol so that it is in total 52 % of the emitted mass. The resulting geographical distribution of the organic fraction in the accumulation mode is shown in Figure 1 (a).

In the physically based approach of Burrows et al. (2014), the organic fraction is computed using the sea surface concentrations of five different classes of macromolecules: proteins, polysaccharides, lipids, processed compounds, and humics. For the macromolecule $i$ having molar concentration $C_i$, the fractional surface coverage $\theta_i$ is given with

$$ \theta_i = \frac{\alpha_i C_i}{1 + \sum_j \alpha_j C_j}, $$

where $\alpha_i$ is the Langmuir coefficient. The total organic fraction in the accumulation mode is then acquired as

$$ F = \frac{\sum_i 2\theta_i M_i}{\sum_i 2\theta_i M_i + \rho_W l s}, $$

where $M_i$ is the molar mass and $a_i$ the specific area of macromolecule $i$ while $l$ is the bubble film thickness, $\rho_W$ the density of sea water, and $s$ the salinity. The required parameters are set as in Burrows et al. (2014). In the coarse mode, we emit organic aerosol so that it is in total 52 % of the emitted mass. The resulting geographical distribution of the organic fraction in the accumulation mode is shown in Figure 1 (b).

Figure 1: Organic fraction of the SSA during the months September, October, and November (SON) as calculated using (a) the parametrisation of Vignati et al. (2010) and (b) the parametrisation of Burrows et al. (2014).
RESULTS AND DISCUSSION

We carried out three simulations using different approaches for the organic fraction of the SSA: the Vignati et al. parametrisation, the Burrows et al. parametrisation, and a baseline approach with no organic SSA emitted. The simulations spanned one year and were performed using the ECMWF ERA-Interim meteorologies for the year 2005. Each simulation had a spinup period of six months.

Figure 2 shows the geographical distributions of the primary marine organic emissions produced by the parametrisations in our simulations. The largest impact of the inclusion of an organic fraction to SSA can be seen on the Southern Ocean. An additional area of large organic emissions can be seen between Alaska and the eastern parts of Russia. Both organic SSA parametrisations produce similar results overall.

![Figure 2: Organic emissions during SON as produced by the simulations utilising (a) Vignati et al. (2010) parametrisation and (b) Burrows et al. (2014) parametrisation.](image)

The zonal mean loading of the simulated organic aerosol, as shown in Figure 3, displays similar features as the emissions. The largest effect relative to the simulation with no organic SSA can be seen around the Southern Ocean. Between latitudes 40° south and 60° north, the effect of non-marine sources is much larger than the marine sources. The Vignati et al. (2010) parametrisation is seen to produce larger organic loading at all latitudes compared with the Burrows et al. (2014) parametrisation.

![Figure 3: Zonal load of particulate organic matter in the simulations during SON.](image)
CONCLUSIONS

We implemented the parametrisations of Vignati et al. (2010) and Burrows et al. (2014) for the organic SSA to the global chemistry transport model TM5. Three different simulations were carried out for the year 2005 in order to assess the effect of additional organic emissions. The results show a clear increase in organic emissions and loading on the Southern Ocean. The parametrisation of Vignati et al. (2010) was observed to produce larger organic emissions overall.

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REFERENCES


EFFECTS OF SOURCE AND PRECIPITATION ON LONG-RANGE TRANSPORTED AEROSOL PARTICLES IN MALDIVES

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Keywords: AEROSOL PARTICLE, PRECIPITATION, BACK TRAJECTORY, TROPICS.

INTRODUCTION

The Earth’s atmosphere contains water in all three phases – vapour, liquid droplets and ice crystals. Water plays a major role in atmospheric processes, is a medium for energy and mass transfer, and is also the most significant greenhouse gas. Many physical and chemical properties of aerosol in the atmosphere are intertwined with water. Atmospheric particles take up different amounts of water with respect to the ambient relative humidity depending on their size and composition. Thus, aerosol particles have a major impact on the climate.

A significant removal process of aerosols from the atmosphere is wet deposition. Wet deposition is the removal process by which aerosol particles are removed from the atmosphere with raindrops. The efficiency of this process depends on the precipitation intensity, aerosol particle sizes, and other microphysical properties. Particle scavenging processes are still a major question mark in atmospheric models (Liu et al., 2012).

To study the effects of aerosol wet scavenging processes, we analysed data measured at an observatory established on Hanimaadhoo, Republic of Maldives, as part of the Atmospheric Brown Cloud (ABC) project. We used k-means clustering on data measured with a Scanning Mobility Particle Sizer (SMPS), and calculated back trajectories for the different clusters using the HYSPLIT 4.9 model. We compared the size distributions of different clusters to the precipitation intensity calculated along the trajectory provided by the model. The results reveal different particle size distributions depending on the source of aerosol particles and precipitation intensity en route to the measurement site.

METHODS

Measurements were conducted at one of the ABC observatories, the Climate Observatory of Hanimaadhoo in Maldives (Ramana and Ramanathan, 2006; Ramanathan et al., 2007). The observatory is located in the northern part of Maldives (6°78 N, 73°18 E) on Hanimaadhoo island; the terrain at the measurement site is very flat, the highest point is only 2 meters above mean sea level. The observatory is surrounded by forest, mainly consisting of palm trees. The observatory is a background site for measuring anthropogenic aerosols coming from the Indian subcontinent. During summer, the Maldives is under the influence of the Indian monsoon, which brings warm and moist marine air consisting mostly of natural aerosols from the Indian Ocean. During winter, which is the dry season, the air masses measured at Maldives are mainly coming from the Indian subcontinent bringing polluted air to the site. The site also experiences a cycle called Madden-Julian Oscillation (MJO), which is an eastward moving low-pressure anomaly at the equator (Madden and Julian, 1971); one cycle lasts 30-60 days.
The measurements were performed during 2004-2008. The year 2007 was excluded as a whole due to lack of data. Fine aerosol particles were measured with SMPS with time resolution of 5 minutes. The size range of the SMPS was 10-500 nm.

To study the effect of air mass origin and precipitation intensity during transport on particle size distribution we used k-means clustering for both original and normalized data (Hartigan and Wong, 1979; Charron et al., 2008). The Dunn index was used to estimate that five clusters were sufficient for further data analysis.

To estimate the origin of different air masses we calculated back trajectories with HYSPLIT model, which is a Lagrangian atmospheric transport and dispersion model. Hourly trajectories and the cumulative rainfall along the trajectory were calculated for the measurement period. The meteorological data, which provided both wind fields and precipitation for the model, was the GDAS 1° dataset from National Center for Atmospheric Research.

CONCLUSIONS

Aerosol particle data measured in Maldives showed distinct clusters in aerosol size distribution shapes (Figure 1). These clusters were attributed to the both different aerosol source regions and the amount of precipitation during transport to the receptor site in different phases of the tropical monsoon and the MJO.
Table 1. Medians of total number concentrations (cm\(^{-3}\)) for original and normalized clustered data.

<table>
<thead>
<tr>
<th>Cluster number</th>
<th>Total number concentration (cm(^{-3})), original data</th>
<th>Total number concentration (cm(^{-3})), normalized data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>153</td>
<td>515</td>
</tr>
<tr>
<td>2</td>
<td>1803</td>
<td>257</td>
</tr>
<tr>
<td>3</td>
<td>2635</td>
<td>808</td>
</tr>
<tr>
<td>4</td>
<td>540</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>918</td>
<td>190</td>
</tr>
</tbody>
</table>

The clustering was done for both original and normalized aerosol particle data. Back trajectories were also calculated for both data sets. Table 1 shows median number concentrations for different clusters. The size distributions of the clusters of normalized data can be seen during different seasons, whereas the deviation of the clusters of original data was clearly dominated by the seasons. Aerosol size distributions were seen to exhibit different characteristics shapes according to the prevailing state of the monsoon and MJO. The trajectories showed different origins for different clusters and variability in the amount of rainfall during the transport to Maldives. During the monsoon, the airflow was mainly from west bringing air masses over the Indian Ocean. During dry season, the air masses were mainly coming from northeast over the Indian subcontinent bringing polluted air to Maldives. The results of the calculated clusters and back trajectories for original data imply that during monsoon (Cluster 1), clean marine air is transported to Maldives, and there is no precipitation along the trajectories but over India. The origin of the air masses of two clusters was the Indian subcontinent. The size distributions of these clusters were mainly measured during dry season. The difference between these clusters was the precipitation intensity during the transport. The last two clusters had properties of pre-monsoon season: the air masses were mainly coming over the ocean, but the clusters experienced different amount of rainfall en route to the site.

ACKNOWLEDGEMENTS

The staff working at the Climate Observatory of Hanimaadhoo is acknowledged for maintenance of the measurements.

REFERENCES


INTRODUCTION

Apart from having an important role in defining air quality, atmospheric aerosols are found to affect the Earth’s radiation budget. The aerosols impact radiation directly by scattering and absorbing incoming solar radiation and indirectly by changing cloud properties via formation of cloud condensation nuclei (CCN) (IPCC 2013). All these impacts are largely affected by the size of the aerosol particles. Thus, studying the parameters involved in the formation and growth of atmospheric particles is essential for understanding their role in our atmosphere. New particle formation (NPF) is found to contribute to at least 50% of the CCN count globally (Merikanto et al. 2009; Kerminen et al. 2012). Freshly-formed clusters are born with diameters of smaller than 2 nm, and they further grow via condensation of available vapors to reach sizes where they can affectively act in modifying atmospheric properties (Dal Maso 2005).

For instance, in order to act as CCN, freshly-formed particles need to grow to a diameter of at least 50 nm and in order to effectively scatter solar radiation, particles need to reach a diameter of 100 nm (Sundström et al, 2015). Sulfuric acid has been found to contribute to the NPF and growth of atmospheric particles. Additionally, oxidation products of biogenic volatile organic compounds (BVOCs) are involved in NPF as well as in the growth of particles formed in NPF (Ehn et al. 2014). Emission of these compounds increases with temperature, which in turn would increase aerosol surface area and thus affect the ratio of diffuse radiation to global radiation, \( R \). Finally, photosynthesis would be affected by changes in this ratio, relating back to the emission of oxidation products of BVOCs, closing the loop.

Satellite measurements would be suitable tools to adopt in studying the effect of aerosols on the amount of radiation reaching the surface. Remote sensing provides information about the spatial distribution of aerosols and trace gases (Sundström et al, 2015), as well as the vegetation structure and photosynthesis, on a nearly global level.

In this study, our aim is to study the aerosol radiation feedback based on satellite data in semi-clean boreal forest in southern Finland.

METHODS

We analysed the aerosol radiation feedback loop presented in Fig. 1. The loop examines the effect of introducing a perturbation of +10ppm in CO2 concentration, first on temperature. The temperature dependence of oxidation products of BVOCs is then investigated. SOA (secondary organic aerosols) concentrations would be affected by any changes to the level of these oxidation products, yet would also directly influence CS (condensation sink) in turn. A ratio of diffuse radiation to global radiation is defined to describe any possible effect on photosynthesis. Finally to close the loop, the approximate nature of CO2 concentration dependency on the level of photosynthesis is examined.
Figure 1. The aerosol radiation feedback loop. Where GPP is gross primary production, SOA is secondary organic aerosols, CS is the condensation sink and R is the ratio between diffuse radiation ($R_d$) and global radiation ($R_g$).

The ground based data that we use in our analysis was obtained from SMEAR (Station for Measurement of Ecosystem-Atmosphere Relations) II measurement station located in Hyytiälä, southern Finland (Hari and Kulmala, 2005). A boreal forest surrounds this station, and major pollution sources are located far away. Long-term measurements of aerosol particle number size distribution are available in this station as well as meteorological quantities and ecosystem measures.

We used several quantities obtained from ground-based measurements that are (presumably) related to the aerosol radiation feedback, and tried to find reasonable satellite retrievals for them. Gross primary production (GPP), which is a measure of ecosystem-scale photosynthesis, was derived from the net ecosystem exchange, primary flux measurement during 1997-2016 (Kulmala et al, 2014). The condensation sink, describing the rate condensable vapors are removed from the atmosphere due to their condensation to aerosol particles (Kulmala et al. 2014), was calculated from particle number size distributions from DMPS (Differential Mobility Particle Sizer). The ambient temperature (T) as well as Global Radiation (0.30 – 4.8 µ) are measured by a mast level of 18 m above canopy. The measurement station also combines different measurements of trace gas concentrations, which might also be later included in our study.

We focused on cloud-free conditions to diminish the effect of clouds (Kulmala et al, 2014). We used included data with the cloudiness parameter greater than 0.8 in our study.

Remote sensing of vegetation by using broadband sensors of vegetation offers vegetation cover indices, such as the normalized difference vegetation index (NDVI) (Tucker, 1979). This index will be used in this study as it correlates well with fraction of photosynthetically active radiation (0.4-0.7 µm) absorbed by the vegetation (FAPAR) (Ranga et al.1997 and Nichol et al. 2000). Surface fluxes data was used from provided data from CERES satellite.

RESULTS
To study the aerosol radiation feedback, correlation between temperature and R was investigated for ground based data in Hyytiälä. As can be seen in Figure 2, there is positive correlation between R and
temperature in Hyytiälä. We considered here days with 90% of data having cloudiness parameter value greater than 0.8.

The relation of R from satellite data with temperature calculated by model for Hyytiälä, can be seen in Figure 3. We found positive correlation between satellite-derived R and re-analysis temperature.

Figure 2: Thirty minutes mean of R as a function of temperature for Hyytiälä. We considered here days with 90% of data having cloudiness parameter value greater than 0.8.

Figure 3: Three hours mean of R from Ceres as a function of re-analysis temperature for Hyytiälä station.

**DISCUSSION AND OUTLOOK**

To study aerosol radiation feedback based on satellite data, we need to investigate the connections between components of aerosol radiation feedback loop for ground based data and satellite-based data.

For achieving our aim of analyzing aerosol radiation feedback loop, temperature and aerosol properties from satellite data will be used. In addition, NDVI/fluorescence offers information about GPP.
Validation of our satellite-based studying will be made by comparing it to the ground-based measured data. For instance, the relation of ratio between diffuse radiation and global radiation with temperature in the boundary layer was studied here.

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IMPACT OF HAZE ON URBAN ENERGY AND WATER BALANCE IN BEIJING

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Keywords: aerosol optical depth, water balance, energy balance, urban.

INTRODUCTION

Simulating urban surface energy and water balances correctly is relevant for a range of applications including numerical weather prediction, air quality modelling and flood prediction. Most of the urban energy and water balance modelling has focused to mid-latitude western countries (e.g. Grimmond et al., 2011), whereas relatively limited amount of studies have been made in Asian newly industrialized countries such as China. In these areas, monsoon circulation strongly determines the local climate and its seasonal variability, and industrialization has brought severe air quality problems. The objective of this study is to examine how well an urban surface energy and water balance model developed based on observations performed in Europe and North America can perform in Beijing and how the haze affects the energy and water balances.

METHODS

Version 2017a of the Surface Urban Energy and Water Balance Scheme (SUEWS) (Järvi et al., 2011; Ward et al., 2017) is used in this study to simulate the energy and water balances in Beijing for 2006–2013. SUEWS has seven surface types (paved, buildings evergreen trees/shrubs, deciduous trees/shrubs, grass, bare soil and water), which are separately simulated but water movements between the surfaces are allowed. Below each surface, except water, there is a single soil layer. In addition to surface characteristics, common meteorological variables are needed to force the model. The forcing data is given to the model in hourly resolution and it is interpolated to the recommended 5-min simulation time step within the model.

The WATCH WFDEI reanalysis product (Weedon et al., 2014) are used to force the model. The spatial resolution of the dataset is 0.5° x 0.5° and the temporal resolution is 3–6 hours. The precipitation of the WATCH data is bias corrected using quantile mapping, and the variables are interpolated to 1 h resolution following methods in Kokkonen et al. (2017).

The model is run for 1 km radius circle around the eddy covariance (EC) measurement tower in Beijing (39.97° N, 116.37° E) (Liu et al., 2012). This area can be used as an approximate source area for the EC measurements that are used to evaluate SUEWS in 2006–2009. The EC setup is located at a height of 47 meters above ground level in a 325-meter high measurement tower and it includes a sonic anemometer (CSAT3, Campbell Scientific) and an open-path infrared gas analyser (LI-7500, Licor Inc.). Hourly fluxes of sensible (QH) and latent heat (QE) were calculated using commonly accepted procedures. Observed meteorological variables are used to evaluate the accuracy of WATCH reanalysis data for Beijing. These include hourly air temperature, wind speed and relative humidity measured at the same EC measurement height, hourly solar radiation from a nearby roof and daily air pressure and precipitation 10 km southeast of the tower.
Surface cover fractions for the study area are derived from aerial photographs using ARCGIS (Figure 1). Separation to evergreen and deciduous trees from the aerial photographs is not possible and here the fractions are based on those obtained from ECOCLIMAP (Masson et al., 2003). Building and tree heights are taken from Liu et al. (2012) and population density from governmental database.

The model is run for 2005-2013, but the first year is used to spin-up the model leaving years 2006-2013 for analysis. The polluted and non-polluted days in the studied years were separated based on aerosol optical depth (AOD, 440 nm) obtained from AERONET station located in Beijing (39.98° N, 116.38° E).

CONCLUSIONS

SUEWS simulates $Q_e$ well, whereas $Q_H$ is systematically overestimated particularly in daytime when the modelled values are on median up to 100 W m$^{-2}$ higher than observations. This overestimation is probably related to the simulation of storage heat flux and/or the net all-wave radiation $Q^*$. With the latter, problems can relate to surface albedo values or problems in simulating the long-wave radiation components, but unfortunately we did not have observations from these. In SUEWS, the downward long-wave radiation is estimated using air temperature and relative humidity and does not currently consider particles in the atmosphere. However, the model performance did not systematically decrease with increasing AOD.

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INTRODUCTION

The particulate matter (PM) emissions from various combustion processes have a well-known direct effect on air quality and routinely observed effect on radiative forcing, yet their indirect contribution to the latter remains less understood. The ice nucleating (IN) efficiency is an important property of particulate matter, because it contributes to formation of cirrus clouds in the upper troposphere and stratosphere, which further affects the atmospheric reflectivity. The IN efficiencies of many natural and anthropogenic PM emissions, both primary and secondary, have not been extensively studied and reported.

Biomass fired cookstoves are widely used for residential cooking in sub-Saharan Africa, due to limited access to electricity in poverty-stricken regions. According to Prasad (2011) 80 % of the sub-Saharan African population use solid fuels in their daily cooking, and most commonly used biofuels are from local tree species. Other typical fuels include agricultural residues, such as husks from coffee beans, sugar cane and rice. Extensive biomass burning causes significant PM emissions that have adverse effects on indoor air quality and human health, but they may also contribute to heterogeneous ice nucleation in the atmosphere.

The IN efficiencies of cookstove emissions were studied using a commercial ice nuclei counter SPIN as a part of the SUSTAINE (Salutary Umeå STudy of Aerosols IN Biomass Cook Stove Emissions) experiment campaign. Experimentation included two types of cookstoves that are commonly used in sub-Saharan Africa, two advanced experimental models, and fuels relevant to the region.

APPLIANCES AND FUELS

The experiment scheme included four different types of cooking appliances, out of which two are commonly used in daily cooking in sub-Saharan Africa and two are being studied to promote sustainable development. The schematic pictures of cookstoves are presented in Figure 1: the simplest design was the traditional three-stone fire that is a ring of bricks holding the cooking pot above a bonfire. The rocket stove design is also fairly simple one, fuel sticks are loaded on horizontal fuel shelf and natural draft of primary air creates a hot burning flame to the vertical pipe. These appliances were operated on wood sticks originating from *Casuarina equisetifolia* and *Sesbania sesban*, both indigenous to large areas in sub-Saharan Africa.
More sophisticated designs included two gasifier stoves, one using natural air draft and the other equipped with an adjustable fan to force primary and secondary air flows to allow a more efficient burn-out of soot and volatile organic matter. The operating principle of a gasifier stove differs from rocket stove in fuel types and air supply method: the fuel used, i.e. up-graded biomass like pellets or chips, is first gasified using primary air and the wood fuel gas burns on the top of the stove in the secondary air zone. The gasifier stoves were operated on pelletized fuels in this study and they originated from Swedish softwood, coffee husk and sugar cane.

![Figure 1: Schematics of stove designs used in the SUSTAINE campaign. Figure credits to MacCarty et al., 2010.](image)

**EXPERIMENTS AND RESULTS**

The combustion tests were performed as simulated cooking events by applying a modified version of the well-established Water Boiling Test (WBT), where 5 litres of water was boiled in a metal pot for 45 minutes in each experiment. The IN experiments were carried out both transiently during the cooking simulation and after that sampling from a 15m³ stainless steel aerosol chamber. A condensation particle counter (CPC, Airmodus A20) was run parallel to the SPIN and the ice-activated fraction \( \alpha \) was defined as

\[
\alpha = \frac{N_{\text{ice}}}{N_{\text{CPC}}}
\]

where \( N_{\text{ice}} \) is the background-corrected concentration of ice crystals detected by the SPIN and \( N_{\text{CPC}} \) is the concentration of sample particles detected by the CPC. Background correction means subtraction of background counts from measured signal. Following the definitions by Vali et al. (2015) we call freezing in water-sub-saturated icing conditions deposition freezing. When \( RH_{\text{water}} > 100\% \) the ice nucleation occurs in immersion mode because the sample particles are introduced to conditions where liquid formation can be expected prior to freezing. Condensation and immersion freezing modes are indistinguishable in the SPIN.

In transient experiments, polydisperse aerosol was introduced to the SPIN after desiccation to < 5 % relative humidity and dilution to a concentration of ~2500 cc⁻¹. Nine experiments were carried out when sample temperature was kept constant at -32 °C and \( RH_{\text{ice}} \) scanned from 100 % up to 160 %: both natural-draft (ND) and forced-draft (FD) gasifier stoves were tested on pelletized Swedish softwood, Sesbania, coffee husk and sugar cane, and the rocket stove on Casuarina sticks. Two experiments were done at very low temperature of -45 °C, scanning the \( RH_{\text{ice}} \) from 100 % up to 170 %: the tests were done using the FD gasifier on Swedish softwood and coffee husk pellets. The scanned \( RH_{\text{ice}} \) range included both deposition and immersion freezing modes. Ice formation was not observed in any experiment at -32 °C on any tested combination. The two experiments below homogeneous freezing temperature induced ice formation at \( RH_{\text{ice}} = 147.6 \% \) and 154.5 %, which both are above when homogeneous freezing becomes the dominant mechanism at 146.4 %, according to Koop et al. (2000).
The focus of the chamber experiments was to study the IN capability of large soot particles in the immersion freezing mode and therefore the samples were size-selected using a Vienna type DMA (Diffuse mobility analyzer) classifier, aiming to largest particle size available in each experiment, and observed soot concentrations were typically 20-200 cc⁻¹. The experiments were carried out in a constant $RH_{water} = 115\%$ and sample temperature was scanned up and down between -32 °C and -43 °C, the latter being significantly below homogeneous freezing limit. Results from combustion experiments were compared to basic homogeneous freezing experiment on highly diluted 350 nm ammonium sulphate particles, where the ice onset at the SPIN was observed at -37.9 °C when $RH_{water}$ was 115 %. In total, the SPIN took part in 13 chamber experiments which are listed in Table 1. Five experiments represented special conditions with deteriorated stove performance and increased the soot emissions. One of those was with no secondary air supply of the FD gasifier stove, i.e. the “broken stove simulation”. In the other case (three experiments), the cooking pot height was adjusted to quench the flame in a position that generated high soot formation.

Table 1: Summary of chamber experiments performed. Experiments marked with an asterisk were carried out with adjusted pot height. Results marked with plus signs indicate when heterogeneous ice nucleation was observed.

<table>
<thead>
<tr>
<th>Cookstove</th>
<th>Fuel</th>
<th>Sample size (nm)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three-stone</td>
<td>Sesanbana</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>Three-stone</td>
<td>Casuarina</td>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>Rocket stove</td>
<td>Casuarina</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Rocket stove</td>
<td>Casuarina</td>
<td>350</td>
<td>-</td>
</tr>
<tr>
<td>Rocket stove</td>
<td>Casuarina</td>
<td>450</td>
<td>-</td>
</tr>
<tr>
<td>ND gasifier</td>
<td>Swedish softwood pellet</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>ND gasifier</td>
<td>Swedish softwood pellet</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>FD gasifier</td>
<td>Coffee husk pellet</td>
<td>260</td>
<td>-</td>
</tr>
<tr>
<td>Broken stove simulation</td>
<td>Swedish softwood pellet</td>
<td>450</td>
<td>+</td>
</tr>
<tr>
<td>Broken stove simulation</td>
<td>Swedish softwood pellet</td>
<td>500</td>
<td>+</td>
</tr>
<tr>
<td>FD gasifier*</td>
<td>Swedish softwood pellet</td>
<td>400</td>
<td>+</td>
</tr>
<tr>
<td>FD gasifier*</td>
<td>Swedish softwood pellet</td>
<td>450</td>
<td>+</td>
</tr>
<tr>
<td>Three-stone*</td>
<td>Swedish softwood pellet</td>
<td>500</td>
<td>-</td>
</tr>
</tbody>
</table>

The positive results from four experiments, i.e. when heterogeneous ice nucleation was observed, are summarized in Figure 2. The error analysis shows the largest temperature deviation on the sample path in the IN chamber during each experiment, indicating that all onset temperatures are significantly below the one of homogeneous freezing also when instrument uncertainty is being taken into account. It is worth emphasizing that the positive experiments were achieved only in scenarios when either the cookstove or the cooking simulation procedure was intentionally modified, causing deteriorated combustion performance and increased soot emissions.
Ice onset temperatures from positive chamber experiments at $RH_{water} = 115\%$ (see Table 1). The error bars present the largest temperature deviation on sample temperature during the collection of data points. Experiments marked with an asterisk were carried out with adjusted pot height. The shaded area shows temperature range below homogeneous freezing limit observed from SPIN using highly diluted 350 nm AS particles as seeds of droplet formation.

**Figure 2**: Ice onset temperatures from positive chamber experiments at $RH_{water} = 115\%$ (see Table 1). The error bars present the largest temperature deviation on sample temperature during the collection of data points. Experiments marked with an asterisk were carried out with adjusted pot height. The shaded area shows temperature range below homogeneous freezing limit observed from SPIN using highly diluted 350 nm AS particles as seeds of droplet formation.

**SUMMARY AND CONCLUSIONS**

The IN capabilities of emissions from both traditional and improved biomass-fired cookstoves were studied using a commercial ice nuclei counter SPIN in the SUSTAINE experiment campaign. Heterogeneous ice nucleation was not observed in any transient experiment on polydisperse sample aerosol at temperatures of -32°C and -45°C up to $RH_{ice} = 160\%$, from which it can be concluded that fresh emissions from the studied cookstoves have a very low IN potential in general. In addition, heterogeneous ice nucleation was not observed in most chamber experiments. This may be explained by the very low size-classified soot concentrations applied in this study, or specific particle properties not accounted here.

However, the IN potential of large soot particles was observed in immersion freezing mode during experiments where the burning conditions were modified with deteriorated stove performance and thus elevated soot emissions. This study indicates that the fresh emissions from both traditional and improved cookstoves, operated according to standardized laboratory procedures, appear to have a very low IN potential. Some IN activity was observed, however, under certain conditions with considerably and intentionally deteriorated stove performance. Further research is therefore needed to elucidate which specific properties of the biomass soot particles are of relevance and under which conditions these occasions might occur. Overall, the relevance of these observations for real-life use of different biomass-fired cookstove solutions should be explored to enable an overall assessment of IN effects of this kind of emissions on a global perspective.

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EDDY COVARIANCE MEASUREMENTS OF CARBON DIOXIDE AND ENERGY FLUXES AFTER CLEARCUTTING IN A DRAINED PEATLAND FOREST

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Keywords: logging residue, carbon cycle, turbulent fluxes, Bowen ratio

INTRODUCTION

The most common method of forest management in Finland is rotation forestry including clearcutting and forest regeneration. Traditional clearcutting involves removing stem wood and leaving logging residues like foliage, branches, stumps and roots on the site. Removing the trees changes the local microclimate: for example, more solar radiation reaches the soil surface, which increases soil temperatures (Londo et al., 1999) and their diel variation. This affects the carbon cycle, as higher soil temperatures potentially increase soil respiration. In peatland forests, however, the enhanced respiration is balanced by the fact that removing tree biomass, which diminishes evapotranspiration, raises the water table level (WTL) (Sarkkola et al., 2010). This slows the peat decomposition rate due to reduced volume of aerated peat. On the other hand, total photosynthesis is diminished due to the removal of trees and destruction of ground vegetation. Also, the above- and belowground logging residue is known to have an enhancing effect on carbon dioxide (CO₂) emissions (Mäkiranta et al., 2012). As slowly growing tree species dominate in the boreal zone, it may take more than 20 years to turn the forest back to a net carbon sink (e.g. Schulze et al., 1999; Hyvönen et al., 2007). However, in ecosystems with high productivity – the site may turn to C sink even within a year after clearcutting (Hyvönen et al., 2007). In this study, we investigated the impact of clearcutting on carbon and energy fluxes at a forested peatland in Finland.

METHODS

Our study site is a nutrient-rich drained peatland ‘Lettosuo’ located in Tammela in southern Finland. The original fen was drained for forestry in 1969 and fertilized with phosphorous and potassium. In 2009, the tree stand at the site consisted of a mixture of Scots pine (75% of the biomass), Norway spruce and Downy birch. Clearcutting was performed within a trapezoidal area (~1.54 hectares) between 29 February 2016 and 16 March 2016. After clearcutting, the soil surface was covered with logging residue and tree stumps, replacing the previous ground vegetation which got destroyed during the clearcutting process. Mounding was performed on 1-2 August 2016, and the seedlings were planted in summer 2017.

An eddy covariance (EC) system was set up in the north-east corner of the clearcut area approximately three weeks after the clearcutting. The EC system included a three-axis sonic anemometer (uSonic-3 Scientific, METEK, Elmshorn, Germany), installed at 2 m from the soil surface, and a closed-path infrared CO₂/H₂O analyser (LI-7000, Licor Biosciences, Lincoln, NE, USA). Ground heat flux and auxiliary meteorological variables, such as air and soil temperatures, WTL and radiation parameters, were conducted about 100 m south of the EC mast, at the center of the clearcut. In addition to this EC system, there is a 25 m tall EC tower at Lettosuo, which has produced above-canopy CO₂ flux data since 2009. This system enables comparison to the conditions before the clearcutting.

Half-hourly fluxes were calculated and post-processed using standard methods (Aurela et al., 2015). For gap filling the growing season flux time series, the net ecosystem exchange (NEE) was partitioned into gross primary production (GPP) and total ecosystem respiration (Reco) (Lloyd and Taylor, 1994). From 1 November 2016 until 8 March 2017, the period with no significant CO₂ uptake, a 5-day moving average was used to fill the gaps in the data.
RESULTS

A significant increase in WTL after the clearcut could already be seen in May, as WTL did not decrease after the spring flood as it typically does. By the end of the summer, WTL rose by 22 cm, reaching a level of -20 cm. The soil temperatures at 20 and 30 cm depths increased by about 1 °C as a result of the clearcut.

From April 2016 to March 2017, the annual CO₂ balance of the clearcut area was 2.9±0.3 kg CO₂ m⁻² yr⁻¹. A comparison of this estimate with the measurements covering the six years before the clearcutting shows that the clearcut turned the CO₂ balance from neutral to a large source. This is due to an 80% decrease in the magnitude of GPP after the clearcutting (data not shown), following the removal of photosynthesizing trees and destruction of the ground vegetation. In addition, R_{eco} decreased by 25%, even though the year after the clearcutting was warmer than the previous year and despite the fact that logging residues were left at the site. The lower R_{eco} could be attributed to a decrease in plant respiration and the increased WTL, which decreases the soil peat decomposition rate and thus results in lower soil CO₂ emissions. One year after the clearcut the GPP had already slightly recovered, showing almost twice as high values of photosynthesis as compared to the first summer (Fig. 1).

Bowen ratio, defined as the ratio of the monthly mean sensible (SH) and latent (LE) heat fluxes, decreased during the summer from 2.4 in May to 0.8 in August (Fig. 2). Latent heat flux was quite stable during this period, so the change in Bowen ratio was caused by the decrease in sensible heat flux, which was associated with the lowering net radiation. These dynamics were most probably due to an increase in albedo as a sparse grass and moss layer developed during the course of the summer. Monthly energy balance closures during summer varied within 80–85%, peaking in September at 90%.

![Figure 1. Time series of daily mean net ecosystem exchange (NEE, top panel), gross primary production (GPP, middle panel) and ecosystem respiration (R_{eco}, bottom panel) measured at the clearcut site from April 2016 to August 2017.](image-url)
Figure 2. Diel variation of net radiation (black, $R_n$), ground heat flux (green, $G$), latent heat flux (blue, LE) and sensible heat flux (red, SH) from May to August 2016.

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INTRODUCTION

Approximately 35% of the world’s forest area is covered by northern boreal forests, ranging in Canada, Alaska, Russia and Northern Europe (Kim & Tanaka, 2003). They have an important role in global carbon (C) balance as they contain about 66% of the world’s forest soil C pools (Kasischke & Stocks, 2000), and changes in these pools would have significant impacts on the greenhouse gas (GHG) balance of the atmosphere. Generally these ecosystems are C sinks, absorbing atmospheric carbon dioxide (CO₂) and releasing it slowly from decomposing organic matter. The occurrence of permafrost makes these high latitude ecosystems especially vulnerable to changing climate (Kim & Tanaka, 2003), as the decomposition may increase under warming conditions (Grosse et al., 2011), and the thawing of permafrost can cause the reduction of soil moisture through increased soil drainage which affects the fluxes of main GHGs (Zona, 2016). As a result of climate warming the occurrence of forest wild fires, one of the predominant natural disturbances in boreal forests, is expected to increase (Kim & Tanaka, 2003). Severe wildfires have also been found to accelerate the degradation of permafrost (Burn, 1998), and further succession of the areas is likely to be modified by permafrost decline. Thus, the increase of severe forest fires and shorter fire return intervals in the area has led to an increase in the distribution of younger stands and decrease in the C storage.

Although the effect of fire on permafrost forest areas has evoked interest of scientists for a rather long time, the changes in uptake and emissions of different GHGs caused by forest fire are less investigated. We investigated a chronosequence of forest fires in northern boreal coniferous forests with permafrost base in north-western part of Canada. Areas with differing time periods since last forest fire, and with comparable ecological conditions, were chosen for testing the impact of fire on CO₂, methane (CH₄) and nitrous oxide (N₂O) fluxes and their recovery after the fire.

METHODS

Our study areas were located along with the Dempster Highway, close to Eagle Plains (Yukon) (66°22’ N, 136°43’ W) and Tsiigehtchic (NWT) (67°26’ N, 133°45’ W) Canada (Köster et al., 2017). In the summer of 2015, four different study areas with different time since the last forest fire (age class) were established: areas with last forest fire in 2012, 1990 and 1969, and control area with no fire for at least 100 years. The ecosystem where our study areas were located is taiga dominated by evergreen needle-leaved trees, Picea mariana (Mill.) BSP and Picea glauca (Moench) Voss. The presence of permafrost slows down litter decomposition and creates nutrient-poor habitats.

Hierarchical sampling procedure was adapted in our study areas. At each age class we established three 150 m-long-lines with three sample plots on line. The lines were located by at least few hundred meters from each other and the sample plots on the line 50 meters apart from each other (all together we had nine
sample plots per age class). The lines were placed in the terrain so that they were at least 150 m from the nearest road to avoid the disturbance of the road on the snow cover and consequently on permafrost. In each line, the measurements of stand characteristics were done on three sample plots (400 m²). The static chamber method was employed for measurements of CO₂, CH₄ as well as N₂O fluxes between the soil and the atmosphere. Gas flux measurements were done during the summer of 2015 on metal collars (on 18 collars per fire age class with diameter 0.21 m and height 0.05 m) installed to the soil before measurements. The vegetation inside the chamber was not damaged or removed during the measurements. A cylindrical chamber (h=0.24 m and Ø=0.20 m) covered with aluminum foil (to prevent photosynthesis), was used in the flux measurements. The CO₂ concentrations inside the chamber were recorded with a non-dispersive infrared CO₂ probe (GMP343, Vaisala Oyj, Helsinki, Finland) and the relative humidity and temperature with RH-/T-sensor (HMP75, Vaisala Oyj, Helsinki, Finland) at 5 sec intervals for 4 min during the 5 min chamber deployment time. The CH₄ and N₂O flux measurements were done using the same chamber as in the CO₂ efflux measurements. For the air sampling the chamber was equipped with an outlet tube that could be closed and opened with a 3-way valve (BD Connecta TM Stopcock, Becton Dickinson, NJ, USA). The CH₄ and N₂O gas samples were collected from the chamber headspace by connecting a 50 ml polypropylene syringe (BD Plastipak 60, BOC Ohmeda, Helsingborg, Sweden) equipped with a similar 3-way valve to the outlet tube of the chamber. Air samples were collected before the chamber placement (0 min) and 1, 5, 10 and 20 minutes after the chamber was placed on the collar and injected immediately into glass vials (12 ml Soda glass Labco Exetainer®, Labco Limited, UK) for storage and transportation. The samples were analyzed by an Agilent Gas Chromatograph model 7890A (GC, Agilent Technologies, USA).

**CONCLUSIONS**

Our study showed that the time passed from last forest fire has a long lasting impact upon all investigated experimental factors (Köster et al., 2017). Soils were warmer and drier, and soil C content was lower on recently burned areas. The depth of the active layer on top of permafrost was increasing rapidly after the fire. The thawing of near-surface permafrost directly affected the GHG fluxes (Köster et al., 2017). Soil CO₂ efflux decreased shortly after the fire, but increased then rapidly. Subarctic boreal forests acted as sinks of CH₄ in our study, but changes in CH₄ fluxes lasted for a short period of time as the uptake of CH₄ did not differ between the areas burned in 1969 and the control areas. A slight decrease in N₂O emission could be observed in comparison of different fire age classes. Based on mixed model analysis on the factors effecting GHG fluxes was the time passed from last forest fire.

**ACKNOWLEDGEMENTS**

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GRAZING BY REINDEER IN NORTHERN BOREAL FORESTS – HOW IT IS AFFECTING GREENHOUSE GAS EMISSIONS FROM FOREST FLOOR

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Keywords: GRAZING, GREENHOUSE GASES, MOSSES, LICHENS.

INTRODUCTION

Reindeer (Rangifer tarandus L.) are the most important large mammalian herbivores in northern latitudes, strongly influencing Arctic lichen-dominated ecosystems (Väre et al., 1996; Köster et al., 2013; Akujärvi et al., 2014). In Scandinavia, more than 35% or approximately 415 000 km² of the land area is grazed by reindeer (36% and 122936 km² in Finland). In Russia, with approximately half of the world’s reindeer population, approximately 20% of the total land area is influenced by reindeer grazing (Jernsletten & Klokov, 2002). If North America is also included, grazing by reindeer influences most of the arctic and subarctic regions, where also the strongest changes caused by climate change are expected (Anisimov et al., 2007).

Little is known about reindeer and their impact on greenhouse gas (GHG) emissions between the soil, ground layer and atmosphere in northern boreal coniferous forests. Ground vegetation, including cryptogamic covers, can fix large amounts of nitrogen (N) and carbon dioxide (CO₂) from the atmosphere (Elbert et al., 2012), but lately it has been shown to also be a large source of nitrous oxide (N₂O) and a small source of methane (CH₄) (Lenhart et al., 2015). This finding combined with grazing may significantly affect the GHG dynamics of Arctic ecosystems.

We have investigated the influence of reindeer grazing on soil GHG (CO₂, CH₄ and N₂O) fluxes, ground vegetation coverage and biomass, soil temperature and water content in northern boreal subarctic coniferous forests. Here we show that grazing by reindeer significantly affects the GHG fluxes.

METHODS

Our study was conducted in northern boreal subarctic coniferous forests, at the Värriö Strict Nature Reserve (67°46' N, 29°35' E) in Finnish Lapland. The study sites are situated north of the Arctic Circle, near to the northern timberline, at an average altitude of 300 m. The study sites are located in the zone of the last intact forest landscapes in Fennoscandia, where large areas of relatively undisturbed subarctic Scots pine (Pinus sylvestris L.) forests can still be found. The study sites belong to the Pohjois-Salla reindeer herding district with approximately 2.2 reindeer per km² (Turunen et al., 2016).

We established the experiment as a split plot experiment with two blocks and five plots. According to the split-plot design, each plot was divided into a grazed and non-grazed subplot separated by a fence. These subplots (n=10) were situated along the borderline between Finland and Russia, where the non-grazed area has been excluded from reindeer grazing nearly a century ago. Our study sites were homogeneous.
The CO₂, CH₄ and N₂O fluxes between the soil and atmosphere were measured using the static chamber method (Pumpanen et al., 2004). Gas flux measurements were performed on 50 polyvinyl chloride (PVC) collars (five collars per plot; diameter 0.22 m and height 0.05 m) installed permanently in the soil during the spring of 2013 (to avoid the possible disturbance by collar installation and biased data, the collars were installed one year before the actual measurements). The measurements of the three GHGs were performed once monthly (in June, July and August) during the growing season of 2014. The chamber used in the measurements was portable (0.24 m in height and 0.22 m in diameter); made of Plexiglass, covered with aluminium foil to keep the interior dark (Pumpanen et al., 2015).

The CO₂ concentration was recorded during a 5-minute chamber deployment time at 5-sec intervals with a diffusion type CO₂ probe (GMP343, Vaisala Oyj, Vantaa, Finland), and air humidity and temperature were measured with a relative humidity and temperature sensor (HM70, Vaisala Oyj, Vantaa, Finland). The CH₄ and N₂O flux measurements were performed separately from the CO₂ efflux measurements. We used the same collars and the same chamber as in the CO₂ efflux measurements, but for the air sampling the chamber was equipped with an outlet tube that could be closed and opened with a 3-way valve (BD Connecta TM Stopcock, Becton Dickinson, NJ, USA). The CH₄ and N₂O gas samples from the chamber headspace were collected using a 50-ml polypropylene syringe (BD Plastipak 60, BOC Ohmeda, Helsingborg, Sweden) connected to the chamber (Köster et al., 2015a). Air samples were collected into the syringe before the chamber placement (0 min) and 1, 5, 10 and 15 min after the chamber was placed on the collar and injected into glass vials (12 ml Soda glass Labco Exetainer®, Labco Limited, UK) for storage and transportation. The samples were analysed by an Agilent Gas Chromatograph model 7890A (GC, Agilent Technologies, USA). The CO₂, CH₄ and N₂O fluxes were calculated using a linear regression between the time and concentration change within the chamber headspace.

Soil temperature and moisture content were measured concurrently with the GHG measurements. During the GHG measurement, volumetric soil moisture content in the top five cm of soil was measured with a portable soil-moisture logger (HH2, Delta-T Devices, UK) with a sensor (ML2, Delta-T Devices, UK). Soil temperature was concurrently also measured with a soil temperature probe (P 300w Temp., Dostmann Electronic GmbH, Germany). In addition, soil temperature during the growing season was measured continuously on every subplot at 3-hour intervals with iButton temperature sensors (Maxim Integrated, San Jose, California, U.S.A.), and soil moisture was continuously registered in two subplots with a ThetaProbe ML2x soil moisture sensor (Delta-T Devices Ltd., Cambridge, England) installed under the organic layer.

CONCLUSIONS

Our study showed that grazing by reindeer significantly affected lichen and moss biomasses in northern boreal forests. Lichen biomass was significantly lower in the grazed areas compared to non-grazed areas. Our results indicated that grazing by reindeer in the northern boreal forests affects the GHG emissions from the forest floor and these emissions largely depend on changes in vegetation composition. Soil was always found to be a source of CO₂ and soil CO₂ emissions were significantly smaller in non-grazed areas compared to grazed areas, mainly being affected by soil temperature. The soils in our study areas were CH₄ sinks through entire measurement period, and grazed areas consumed more CH₄ compared to non-grazed areas. We also observed that the N₂O emissions were significantly affected by moss biomass and soil temperature. Non-grazed areas with lower moss biomass and soil temperature were a small sink of N₂O while the total fluxes remained around zero in the grazed areas. Time of measurements was also influencing the GHG fluxes. In June and August there were significant differences in CH₄ and CO₂ fluxes between the grazed and non-grazed areas, as the grazed areas were bigger sinks for CH₄ and emitted more CO₂. In July, there was no statistically significant difference between grazed and non-grazed areas in CH₄ and CO₂ fluxes.
ACKNOWLEDGEMENTS

This work was supported by grants from the Kone Foundation and the Academy of Finland projects (grants nr. 307222, 294600, 286685). We also acknowledge the staff of Värriö Research Station supported by the Academy of Finland Center of Excellence programme (grant no. 307331).

REFERENCES


REMOVAL OF SEMI-VOLATILE COMPOUNDS FROM THE ATMOSPHERE

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Key Words: Semi-volatile Compounds, UCLALES-SALSA, Wet Removal, Aerosols.

INTRODUCTION

The effect of aerosols on the Earth’s energy budget has been a subject of research for a relatively long period of time, however, the anthropogenic effect of aerosols still poses huge uncertainties in the prediction of our future climate (Lohmann and Feichter, 2005). One of the sources of these uncertainties is the representation of global distribution of aerosols which is not properly treated in climate models. Removal of aerosol by wet deposition is a key process governing aerosol transport and distribution, yet it is often omitted or poorly represented in global models. Exacerbating the problem is the modification of aerosol distributions by semi-volatile compounds such as ammonia and nitric acid which has comparatively received little attention. A crucial property of semi-volatile compounds is that they deposit onto pre-existing aerosol particles potentially forming super-micron sized aerosol particles even at sub-saturated environments and hence modifying aerosol distributions and hygroscopicity (Kokkola et al., 2003).

In this study we use a state-of-the-art LES model UCLALES-SALSA (Tonttila et al., 2017) comprising an interactive aerosol-cloud scheme SALSA (Kokkola et al., 2008), which tracks aerosols through all processes that modify aerosol distributions such as cloud activation and processing, precipitation formation and droplet evaporation to assess how semi-volatile compounds affect aerosol distribution and how effectively they interact and are removed from the atmosphere by wet processes. SALSA is a bin-system microphysics model that comprises a detailed description of aerosols, clouds and precipitation. In addition to standard vapor condensation and coagulation of aerosol particles, SALSA has also been recently upgraded to treat key microphysical processes such as the dissolution of semi-volatile gases e.g. $HNO_3$ and $NH_3$. The bin system in SALSA is configured in such an innovative way that the cloud bins are parallel to those dry sizes of condensation nuclei. This approach is meant to accurately resolve the evolution aerosol size distribution which is strongly affected by cloud activation, cloud processing and evaporation. This is a key feature for accurately representing particle size distributions, which are important in climate modeling.

METHODS

A new condensation routine has been incorporated into SALSA to include the condensation of semi-volatile compounds ($HNO_3$ and $NH_3$) onto aerosol and water droplets.
Two schemes, the Analytical Predictor of condensation (APC) and the Analytical Predictor of Deposition (APD) of Jacobson (2005) are used to treat condensation in this new scheme. The APC scheme is applied only for vapor condensation in supersaturated conditions, while the APD is applied for water vapor in subsaturated conditions and for the gases in all conditions.

The APC scheme works by defining the rate of change of particle phase concentration of species \( q \) in size bin \( i \) and time instant \( t \) as \( \frac{dc_{q,i,t}}{dt} \) given by:

\[
\frac{dc_{q,i,t}}{dt} = \kappa_{q,i,t-h}(C_{q,t} - S'_{q,i,t-h}C_{q,s,i,t-h}) \tag{1}
\]

Where, \( \kappa_{q,i,t-h} \), is defined as the mass transfer coefficient at previous time step \( (t - h) \), \( C_{q,t} \), as the total gas phase concentration in the current timestep, \( S' \) is the equilibrium saturation ratio, \( C_{q,s,i,t-h} \) is the saturation vapor mole concentration in the previous timestep. By integrating equation (1) a noniterative solution to the growth equation can be determined.

\[
c_{q,i,t} = c_{q,i,t-h} + h\kappa_{q,i,t-h}(C_{q,t} - S'_{q,i,t-h}C_{q,s,i,t-h}) \tag{2}
\]

Since \( C_{q,t} \) in equation (2) is currently not known, it can be resolved by assuming mass conservation, i.e. that the sum of particle phase and gas phase concentration in the previous time step is equal to the same in the current time step. This leads to equation (3) where all terms on the right hand side of the equation are resolvable from the previous timestep and \( C_{q,t} \) can then be used in equation (2).

\[
C_{q,t} = \frac{C_{q,t-h} + h \sum_{i=1}^{N_R} (\kappa_{q,i,t-h}S'_{q,i,t-h}C_{q,s,i,t-h})}{1 + h \sum_{i=1}^{N_R} \kappa_{q,i,t-h}} \tag{3}
\]

On the other hand, the rate of change of particle phase concentration of species \( q \) in size bin \( i \) and time instant \( t \), \( \frac{dc_{q,i,t}}{dt} \) for the APD scheme is given by:

\[
\frac{dc_{q,i,t}}{dt} = \kappa_{q,i,t-h}(C_{q,t} - S'_{q,i,t-h}C_{q,t}) \tag{4}
\]

Where \( H_q \) is the Henry’s constant, often unit for undissociated dissolved gases and the other variables have the same definitions as in the APC. By integrating (4) we get the particle phase concentration as,

\[
c_{q,i,t} = H'_{q,i,t-h}C_{q,t} + \left( c_{q,i,t-h} - \frac{H'_{q,i,t-h}C_{q,t}}{S'_{q,i,t-h}} \right) \exp\left(-\frac{hS'_{q,i,t-h}\kappa_{q,i,t-h}}{H'_{q,i,t-h}}\right) \tag{5}
\]

while applying mass conservation for species \( q \) between the current and the previous time steps as in the condensational growth, we resolve the unknown \( C_{q,t} \) as:

\[
C_{q,t} = \frac{C_{q,t-h} + \sum_{i=1}^{N_R} \left\{ c_{q,i,t-h} \left[ 1 - \exp\left(-\frac{hS'_{q,i,t-h}\kappa_{q,i,t-h}}{H'_{q,i,t-h}}\right)\right]\right\}}{1 + \sum_{i=1}^{N_R} \left\{ \frac{H'_{q,i,t-h}}{S'_{q,i,t-h}} \left[ 1 - \exp\left(-\frac{hS'_{q,i,t-h}\kappa_{q,i,t-h}}{H'_{q,i,t-h}}\right)\right]\right\}} \tag{6}
\]
RESULTS AND DISCUSSION

![Graphs showing particle wet radii and volume concentration](image)

Figure 1: The snapshots of particle phase volume concentrations of (a) Nitric acid, (b) Ammonia across all aerosol size bins. The different curves represent concentrations at different times during the simulation. Broken lines; black = 10s, blue = 50s, green = 100s and red = 200s, solid lines; black = 500s, blue = 1000s, green = 2000s and red = 4000s

These two schemes have been implemented in the 1-D version of SALSA and their performances have been tested in a closed system in both subsaturated and saturated conditions to assess the behavior of the semi-volatile compounds. The relative humidity was raised from 93% to beyond 100% where particle activation takes place. Temperature and pressure read in from a parcel model are used to force the simulation. A lognormal

![Graphs showing gas-phase and particle-phase concentration of semivolatile gases](image)

Figure 2: Time evolution of gas-phase and particle-phase concentration of semivolatile gases.

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distribution was assumed for the aerosol distribution with the total aerosol concentration of 100 cm$^{-3}$ and a standard deviation of 2 while the median mean diameter was 0.8 µm. Figure 1 shows the snapshots of particle phase volume concentrations of (a) Nitric acid, (b) Ammonia across all aerosol size bins taken at different time times during the simulation. What the figures show is that the particle phase concentrations are distributed evenly following the original aerosol mass distribution (not shown). The last two curves, the solid green taken 2000s and the red taken at 4000s were taken after the air parcel was saturated hence it shows the sudden increase in particle sizes due to particle activation.

Figure 2 shows the time evolution of the total gas-phase and particle-phase concentrations of semi-volatile gases in a closed system. It is apparent that the gas-phase concentrations are almost depleted within half an hour into the simulation. This was a short simulation hence the evaporation of the gases from the particle phase back to the gas phase concentration was not produced in this simulation. It is expected that the at some point the particle-phase gases evaporate back in the gas-phase as they try to establish a thermodynamic equilibrium with the gas-phase. An indication of this behavior is shown in the forth bin of figure 3 where the particle size of that bin clearly decreases due to evaporation.

CONCLUSIONS

The ongoing work is set to be implemented in UCLALES-SALSA where we intend to asses the effectiveness of the removal of these compounds by wet deposition. The preliminary results have shown successful implementation of this scheme in 1-D simulation version of SALSA, where a significant modification of the aerosol size distribution was noted well below saturation. This implies more aerosol particles will be large enough to be activated into cloud droplets in addition to changing the hygroscopicity and hence affect cloud microphysical properties.
ACKNOWLEDGEMENTS

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References


Efficacy of Black Carbon Mitigation in Slowing Arctic Warming

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Keywords: Arctic, black carbon, climate modelling, aerosol.

INTRODUCTION

Although global warming has been recognised as one of the main concerns of the 21st century, mitigation measures are only slowly being implemented and greenhouse gas emissions continue to increase. According to the fifth assessment report of the IPCC, the global mean surface temperature is likely to increase by 1.5° or more until the end of the century compared to pre-industrial times. In the Arctic, surface temperatures are projected to increase at a much higher rate [Kirtman et al., 2013]. Mitigation of short-lived climate pollutants (SLCP) has been suggested to be an efficient short-term measure to slow arctic warming. The projected 2° increase in 2050 may be decreased by up to 0.5° if maximum SLCP mitigation was implemented globally [AMAP 2015, Stohl et al., 2015], half of which are attributed to reductions in black carbon (BC). However, there are still many sources of uncertainty. For instance, the relative amount of substance reaching the Arctic is usually greater if the source is close by, but on the other hand the emission strengths in the arctic region are already small to begin with, so it is unclear which mitigation measures are most effective and if these should be the same everywhere. Additionally many pollutants are usually co-emitted by one source, so even if only one substance is targeted by a mitigation measure, other emissions will be reduced as well (not all of which may lead to cooling). This makes the overall effect of a mitigation measure hard to assess. Here we investigate how maximum BC mitigation in different regions of the globe affect radiative forcings in the Arctic.

METHODS

We use the aerosol-climate model ECHAM-HAMMOZ (ECHAM6.3-HAM2.3-MOZ1.0) with the aerosol microphysics module SALSA [Bergman et al., 2012] to simulate the near-future impact of BC mitigation strategies on Arctic climate. We use specially generated aerosol emission scenarios, which are based on the ECLIPSE emission inventories. In our study, we compare 5 emission scenarios for the year 2030: (1) the emissions following the current legislation (CLE), (2) CLE + BC mitigation in the Arctic council (AC8) member states, (3) CLE + BC mitigation in AC8 and active observers, (4) CLE + BC mitigation in AC8 and all observers, and (5) CLE + global BC mitigation. The simulation results are compared to a reference simulation for the year 2010. All simulations are run over 30 model years, plus half a year of spin-up. Here we are only interested in aerosol effects, all other parameters, in particular greenhouse gas concentrations, sea surface temperature, and sea ice extent, are held fixed at 2010 values.

Figure 1a shows the reduction in BC emissions for the different scenarios and Fig. 1b shows the resulting change in aerosol clear-sky direct radiative forcing in the Arctic (north of 60° latitude). As can be seen, all
BC mitigation scenarios produce negative (cooling) radiative forcings in the Arctic and the cooling is stronger the more the global emissions are reduced. However, as shown in Table 1, the relative effect that the emission reductions have depends on the distance of the affected emission sources to the Arctic. As an example, implementing the suggested mitigation measures in the Arctic Council alone reduces the global BC emissions by only 4% of the global emissions compared to the current legislation, while aerosol cooling is increased by 11%. Extending BC mitigation to all observer states (which includes China and India) increases the emission reductions 7.5-fold, while aerosol cooling is only four times higher. However, the cooling effects of emission reductions are still substantial also in regions far away from the Arctic.

![Figure 1. Changes in (a) BC emissions and (b) clear sky radiative forcing since 2010.](image)

<table>
<thead>
<tr>
<th></th>
<th>reduction in BC emissions by 2030 relative to CLE</th>
<th>additional aerosol cooling in arctic area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current legislation (CLE)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AC8 SLCP mitigation</td>
<td>-4 %</td>
<td>+11 %</td>
</tr>
<tr>
<td>AC8 + active observers SLCP mitigation</td>
<td>-17 %</td>
<td>+31 %</td>
</tr>
<tr>
<td>AC8 + all observers SLCP mitigation</td>
<td>-30 %</td>
<td>+44%</td>
</tr>
<tr>
<td>Global SLCP mitigation</td>
<td>-71%</td>
<td>+94%</td>
</tr>
</tbody>
</table>

Table 1. Relative changes in BC emissions compared to the relative cooling impact in the arctic region.

CONCLUSIONS

In order to assess the efficacy of black carbon (BC) mitigation in slowing Arctic warming, we performed a set of simulations with different emission scenarios, which implemented BC mitigation measures in a successively larger region of the globe. We find that BC mitigation is most effective in regions that are close to the Arctic. However, as BC emissions close to the Arctic are already relatively low, the full potential of BC mitigation can only be reached if emissions are reduced globally.
ACKNOWLEDGEMENTS

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REFERENCES


THE CARBON DYNAMICS OF BOREAL DWARF SHRUBS DIFFER FROM THOSE OF SCOTS PINE SEEDLINGS

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Keywords: Photosynthesis, autotrophic respiration, NPP, ¹³C labelling

INTRODUCTION

The ground layer of boreal pine forests is vegetated and therefore photosynthetically active. A dense community of plant species consisting of ericaceous shrubs, herbs, grasses, mosses and lichens colonizes the ground of boreal forest ecosystems. The primary productivity of this vegetation is notable (Goulden and Crill 1997, Moren and Lindroth 2000, Kolari et al. 2006, Kulmala 2011). The share of them contributing to CO₂ uptake of a forest ecosystem naturally depends on site and vegetation characteristics but most common annual estimates lay between 10–20 % (Swanson and Flanagan 2001, Ilvesniemi et al. 2009, Bergeron et al. 2009, Kulmala et al. 2011). However, it is still unclear how much of this primary productivity is allocated to long-lived structural compounds or if it is briefly stored and released via root exudates and autotrophic respiration. Thus, it is not known which part of the observed CO₂ emissions at forest floor actually originates from the ground vegetation and which fraction originates from trees and the decomposition of soil organic matter. The aim of this study was to improve the reliability of Scots pine boreal forest carbon balance estimates by quantifying the primary production of the most common species on the forest floor and reveal their carbon allocation patterns.

METHODS

The seedlings of Pinus sylvestris L. (Pinsyl), Vaccinium vitis-idaea L. (Vacvit), Vaccinium myrtillus L. (Vacmyr) and Calluna vulgaris (L.) Hull (Calvul) were propagated from seeds. After germination, 14 seedlings of each species were planted in humus-filled microcosms (Pumpanen et al. 2009). 14 microcosms lacking seedlings were established as control treatments. The seedlings grew in a growth chamber with a stable temperature, stable PAR intensity and with a day length of 18 hours for 9 months.

The CO₂ and H₂O exchange rates of the shoots and belowground parts were measured from 8 individuals per species by enclosing them in separate, airtight compartment chambers. The experimental setup is described in detail by Pumpanen et al. (2009). First, we enclosed the seedling in darkness and measured gas exchange of the belowground parts. Then, we measured the aboveground compartment chamber similarly. After measuring the darkened plants, we repeated the same measurements but this time placed a light source in front of the plant. From the gas exchange, we derived photosynthesis, transpiration, water use efficiency, respiration of above ground parts, net primary production and the respiration of roots separately in light and dark conditions (RRlight and RRdark).

Stable isotope labelling took place after the gas exchange measurements. The seedlings were grown in a constant light environment and exposed to ¹³C for two hours per day over a five-day period. After that, plant material was lyophilized, separated into organs (stem, leaves, rhizome, roots), weighted and ground into a fine powder for further analysis. A subsample of each organ was sent to UC Davis Stable Isotope Facility for ¹³C analysis and to former Finnish Forest Research Institute for sugar analysis. Kulmala et al. (2017) has reported the used plant material, growing conditions and the experiments in more detail.
RESULTS AND DISCUSSION

The biomass allocation was similar between the species except for Vacmyr that has annual leaves unlike the other species. Vacmyr allocated 21% of the biomass to the leaves and 31% to the stems whereas those of the other species were 42–52% and 13%, respectively. Calvul had the highest aboveground share (66%) but that of Pinsyl (60%) did not differ significantly. V. aureum are the only species with rhizomes included in this study. Vacit and Vacmyr allocated 15% and 6% of their biomass to the rhizome, respectively. The share of roots did not differ between the species, although the rhizome increased the belowground share of Vacmyr and Vacit.

The distribution of δ^{13}C widely differed from the biomass fractions. The biggest differences were found in roots whose relative share of δ^{13}C was much lower than their relative biomass. The relative distribution of the ^{13}C-label was the highest in leaves decreasing towards roots for all the dwarf shrubs whereas for Pinsyl, the highest share of ^{13}C was in the stem, which at this age is probably due to the plant’s capacity to grow tall trunks.

Pinsyl had the highest rate of photosynthesis, above and belowground respiration and transpiration showing increased metabolism compared with ericoid dwarf shrubs when normalized by total biomass. The belowground CO2 emissions of the dwarf shrubs were very low especially in dark conditions. Scots pine appears to have a particularly high activity caused by either roots or root-associated microflora. The reason for this might relate to its ectomycorrhizal fungi that can be more predominant and large in biomass than the ericoid mycorrhizal fungal association in dwarf shrubs. Vigorous fungi associated with pine could explain the generally high rate of metabolism that limited biomass accumulation. Ectomycorrhizal fungi are a great sink of carbon and for ericoid species, the lack of such strong sink might have down-regulated also photosynthetic activity (Paul and Foyer 2001).

The RR_{dark} of the dwarf shrubs was app. 10–20% of the rate of photosynthesis P whereas for Pinsyl, it was app. 46% of it. Interestingly, the RR_{light} of Pinsyl was of a similar magnitude than RR_{dark}, but for dwarf shrubs, RR_{light} was app. 50–70% higher than that of RR_{dark} (Fig. 1). The reason for this remains unclear but it might be that Scots pine has a better capacity to regulate internal carbon storages than dwarf shrubs allowing rather continuous carbon flow belowground despite the variation in photosynthesis. Another explanation is that the constant activity of root-associated fungi may balance out differences in CO2 output from the ectomycorrhizal roots in light and dark conditions. However, further studies including detailed microbial data is required to support these assumptions.

Pinsyl had the highest transpiration when normalized by total biomass. Vacmyr and Pinsyl had the highest WUE but the values did not significantly differ between the species.

![Figure 1. The ratio between root respiration in darkness and in light conditions in the measured individuals of different species](image-url)
CONCLUSIONS

Our results indicate that despite obvious differences in morphology, young dwarf shrubs have similar rates of above and belowground carbon exchange that differ significantly from those of Scots pine. The root respiration rates of the dwarf shrubs differ greatly in light and dark conditions whereas those of Scots pines seem not to. Larger plants may have different carbon dynamics than the seedlings studied in this microcosms experiment but our results suggest that ericoid plants rapidly allocate fixed carbon to belowground compartments and outside roots. Therefore, much of the soil CO₂ production detected in soil respiration measurements during light hours is likely to be derived from the activities of these species. In contrast, our data suggests that the nighttime soil respiration measurements may better reflect the contribution of the tree root-associated autotrophic respiration. The soil chambers commonly used in the field also include dwarf shrubs. Therefore our data can be used to estimate the contribution of dwarf shrubs to soil CO₂ fluxes allowing a better prediction of the effects of environmental changes on the source and sink capabilities of boreal forest ecosystems.

ACKNOWLEDGEMENTS

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INTRODUCTION

Urban areas are generally characterised by elevated traffic-related air pollutant emissions at pedestrian level. This is also where most of the urban dwellers reside and are thus exposed to decreased air quality. The dispersion conditions of air pollutants are determined by local wind conditions, which in turn are modified by the presence of urban roughness elements, their thermal properties as well as vehicle-induced turbulence near surface. This urban complexity is, however, inadequately represented both by current air quality models and field measurements.

With the current knowledge, we can identify the major air pollutant sources in urban areas, but our ability to understand the spatial and temporal variation is insufficient. A building-resolved air quality modelling tool is needed to support the urban planners in the design of healthier living environments and to provide data with high enough resolution for human exposure studies. Currently, large-eddy simulation (LES) is the most promising method for this purpose.

METHODS

LES simulates the three-dimensional field of motion as well as temperature, humidity and/or other scalar concentrations as a function of time and space. The prognostic Navier-Stokes equations are resolved directly for length scales larger than the model grid resolution, whereas the sub-grid-scale structures are parametrized. In order to directly resolve most of the kinetic energy in urban areas, a grid resolution of 2 m or finer is needed. Hence, LES provides a high-resolution but a computationally intense modelling tool, which requires a supercomputer environment to conduct neighbourhood-scale simulations. The LES model applied here is the Parallelized Large-Eddy simulation Model (PALM, v4.0) (Maronga et al., 2015), which is especially suitable for complex urban environments.

In order to take into account the effect aerosol dynamic processes have on the aerosol particle concentrations, a sectional aerosol module SALSA (Kokkola et al., 2008) has recently been embedded to PALM by the author. SALSA has been optimized for large scale climate models which are computationally expensive. Therefore, the number of size sections is kept to the minimum and only the following chemical components are included: sulphate, organic matter, black carbon, nitrate, ammonium, sea salt and dust. Furthermore, only the most significant aerosol dynamic processes for each size section are considered. SALSA includes the processes of condensation, evaporation, coagulation and hydration along with nucleation using different parametrisations. Also, the impact of dry deposition on tree leaves is included according to the models by Zhang et al. (2001) and Petroff and Zhang (2010).

Preliminary simulations in a simple street canyon with street trees (Figure 1) have been conducted to evaluate the performance of SALSA within the PALM environment. In these simulations, the aerosol size distribution ranges from 3 nm to 10 μm and the number of size sections is set to 10. An invariable background concentration is constantly being advected to the modelling domain whereas traffic
emissions are described by applying a size-dependent aerosol flux to the lowest grid level above car-traffic lanes. Aerosol particles are assumed to consist only organic matter. Simulations were conducted on a personal PC for 20 minutes of which the last 10 minutes was applied to calculate the mean concentrations and wind velocities.

CONCLUSIONS

Figure 1: Simulation set-up for a simple street canyon with street trees in the middle (in green). Car-traffic lanes with a size-dependent aerosol flux is marked in dark red.

Figure 2: a) The mean number concentration $N$ (m$^{-3}$) and wind field averaged over the total length of the canyon, and the relative change (%) in $N$ due to b) coagulation of aerosol particles and c) dry deposition on tree leaves.
Figure 2a displays the accumulation of aerosol particles to the windward side of the canyon due to the formation of a canyon vortex. If coagulation of aerosol particles is allowed (Figure 2b), $N$ is decreased by up to 45% inside the canyon. The decrease is most notable where the wind flow is slowest, i.e. in the middle of the canyon vortex and close to the windward wall. Instead if dry deposition on tree leaves is allowed (Figure 2c), $N$ is again decreased but to a smaller extent. This is explained by the small deposition velocity of the smallest particles which, in turn, represent a majority of the number concentration.

These preliminary simulations will be followed by a comprehensive evaluation study against data from measurement campaigns from different locations.

ACKNOWLEDGEMENTS

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REFERENCES


TRENDS OF ATMOSPHERIC MERCURY AT A SUB-ARCTIC SITE PALLAS IN FINLAND

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Keywords: TGM, trends, emissions.

INTRODUCTION

Mercury (Hg) is one of the most hazardous environmental pollutants due to its toxicity (neurotoxin) and ability to accumulate in the environment. It has an atmospheric lifetime of 0.5–2 years (Schroeder and Munthe 1998), resulting in global dispersion of this component. In this study, total gaseous mercury (TGM) has been measured for twenty years at a sub-arctic site Pallas in Northern Finland. The station is part of many international programs such as WMO/GAW, EMEP, AMAP, IM and GMOS. In general, the air quality at Pallas has improved over the time of the measurements due to decreased emissions in Finland and elsewhere in Europe (Lohila et al., 2015). Here we present the trends of TGM during different time periods.

METHODS

The sampling site is a background station located in Northern Finland (68 N, 24 E). More details of the station characteristics are given in Lohila et al., 2015. Since 1996, TGM has been sampled with a manual gold trap technique by FMI and later analysed by CV-AFS in the laboratory by IVL (Munthe et al., 2007). The manual method utilizes one or two daily samples per week. Later in 2007, a parallel automatic technique was employed by FMI to obtain continuous TGM data. The details of the automatic method using Tekran 2537 Mercury Analyzer can be found in Kyllönen et al. (2012). The trend analysis for concentration data was calculated by Generalized Least-Squares (GLS) regression with classical decomposition and AutoRegressive Moving Average (ARMA) errors applied for monthly mean values (see e.g. Anttila and Tuovinen, 2010). For emission data, the presence of trends was investigated with the application of the Mann-Kendall test and Sen’s slope estimate.

CONCLUSIONS

The atmospheric concentration of mercury at Pallas is at the global background level with annual average values of 1.4-1.5 ng m⁻³ (see Fig. 1).

Figure 1. Atmospheric total gaseous mercury measurements at Pallas in 2008-2015 using automatic measurement technique (hourly values).
The concentration level is rather steady due to minor domestic emissions in the sub-arctic area and long distance to the large European source areas. The observed concentrations are slightly above the concentrations measured at the more southern stations in Hyytiälä and Virolahti, where mercury is continuously measured with Tekran 2537 instruments since 2008 and 2006, respectively. At Pallas, mercury has a seasonal trend with peaks in the late winter due to the higher amount of energy production during that time of the year. During the spring time, very low mercury concentrations have been occasionally recorded when hourly concentrations have dropped down to 0.6 ng m$^{-3}$. This is due to a spring-time phenomenon termed as atmospheric mercury depletion events (AMDE), which is a series of photochemically-initiated reactions in the atmosphere when mercury is scavenged from the atmosphere in the Polar Regions. These depleted air masses sometimes reach Pallas.

The trend analysis showed that atmospheric mercury concentration has not changed at Pallas during the 1996-2014 period (Fig. 2) at all with a flat 0.0 % change. This is concurrent with the development of national mercury emissions, which have not had statistically significant trend during the same period (change 0 %). However, the mercury emissions in Europe (and Northern America) have declined during that time while the emissions in Asia have increased. Additionally, we repeated the trend analysis for a shorter time series of 8 years (2008-2015) to see whether there has been any recent changes in mercury concentration (Fig. 3). Also, the deployment of Tekran analyser in 2008 allowed the use of a continuous time series. During that time period, the result remained the same; no statistically significant trend was recorded. However, the national mercury emissions declined by 28 % (95 % confidence level) during the same time period. This gives indication that global emission reductions are needed to reduce atmospheric mercury concentrations in background areas. In addition, increase of mercury emission from the North Sea due to declining ice coverage may affect the observed mercury concentration at Pallas.

![Figure 2](image2.png)

Figure 2. Atmospheric measured and modelled concentrations (monthly values) with annual trends of total gaseous mercury at Pallas in 1996-2014 (manual method). No trend is detected.

![Figure 3](image3.png)

Figure 3. Atmospheric measured and modelled concentrations (monthly values in ng m$^{-3}$) with annual trends of total gaseous mercury at Pallas in 2008-2015 (automatic method). No statistically significant trend is detected.
REFERENCES


SUB-10 NM AEROSOL PARTICLE LAYERS OBSERVED ALOFT USING INSTRUMENTED AIRPLANE

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Keywords: new particle formation, planetary boundary layer, airborne measurements

INTRODUCTION

Atmospheric new particle formation (NPF) has important implications for health, environment and climate (e.g. Kulmala et al. 2013). Airborne measurements of NPF events in the lower troposphere are scarce but useful in studying for example the role of atmospheric dynamics on the onset and intensity of NPF (e.g. Easter and Peters, 1994).

In order to gain a more complete picture of NPF in the boundary layer and lower troposphere we measured vertical profiles of aerosol particle number concentrations, number-size distributions, meteorological variables and gas concentrations over southern Finland using a Cessna 172 airplane.

METHODS

Seven flight measurement campaigns were conducted between the years 2013-2017 (Väänänen et al., 2016). The campaigns were timed around spring and autumn. Short summary of instruments and measured quantities onboard is given in Table 1.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measured quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Airmodus PSM</td>
<td>Above 1.5 nm particle number concentration</td>
</tr>
<tr>
<td>TSI 3776 CPC</td>
<td>Above 3 nm particle number concentration</td>
</tr>
<tr>
<td>SMPS</td>
<td>10-400 nm particle number-size distribution</td>
</tr>
<tr>
<td>Li-Cor Li-840</td>
<td>CO$_2$ and H$_2$O vapor concentrations</td>
</tr>
<tr>
<td>AIMMS-20</td>
<td>Wind vector</td>
</tr>
<tr>
<td>Meteorological sensors</td>
<td>Static pressure, temperature and RH</td>
</tr>
</tbody>
</table>

Table 1. Summary of instruments and measured quantities onboard the Cessna.

The profiles were flown around the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations; Hari and Kulmala, 2005) station in Hyytiälä, southern Finland. The flight measurements were compared to the station's extensive continuous measurements. Figure 1 shows an example of a flight profile.
We also used data from atmospheric soundings performed in Hyytiälä during the BAECC campaign in 2014 (Petäjä et al. 2016) and from continuous soundings in Jokioinen.

RESULTS

On multiple days we found elevated sub-10 nm particle number concentrations near the interface between the residual layer and the free troposphere (capping inversion). The small size of the particles coupled with the stability of the layer suggests that the particles were recently formed by nucleation in situ.

Figure 2 shows an example from April 4, 2014. A capping inversion left from the previous day's boundary layer had subsided to about 2500 m at the time of the profile (see Fig. 2c). The top of the new convective boundary layer (CBL) was at about 1200 m, which was most clearly visible in the RH profile (see Fig. 2b). Figure 2a shows the particle layer at roughly 2100 m, residing just below the temperature inversion.

Figure 2. (a) profile of 3-10 nm particle number concentration onboard the Cessna, (b) profile of temperature and RH onboard the Cessna and (c) temperature and RH profiles from soundings in Hyytiälä.
Panel (c) shows CBL rising by convection on April 3, 2014 and the inversion left on top subsequently subsiding on April 4, 2014. Panel (b) show the elevated inversion at ~2500 m and the fresh CBL at ~1300 m. Panel (a) shows the nucleation mode particle layer at about 2100 m.

It is still not clear how common the particle layers are or how often they become entrained into the CBL. Further work is being done in order to assess the prevalence and impact of the phenomenon.

DISCUSSION

Our results suggest that separate NPF may happen above the CBL, specifically in the capping inversion where the conditions for nucleation may be particularly favourable due to reduced sinks, low temperatures and mixing at the interface (Nilsson and Kulmala, 1998). The gaseous precursors emitted from the surface could be found in the capping inversion since they are mixed up in the previous day’s CBL. Our results are also supported by some previous observations (Wehner et al., 2010).

ACKNOWLEDGEMENTS

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NANO-CAVA PROJECT – FORMATION OF CLUSTERS FROM ATMOSPHERIC VAPOURS

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Keywords: atmospheric aerosols, nucleation, clusters

INTRODUCTION

New particle formation occurs when vapour molecules collide with each other forming molecular clusters and conditions are favourable for these clusters to stay together and continue growing in the atmosphere. Approximately half of global cloud condensation nuclei result from new particle formation (Merikanto et al. 2009), so understanding this process is relevant for estimating the climate impact of aerosol particles. Since the technologies to measure clusters, their pre-cursor vapours and recently formed particles have become available only recently, we are still lacking knowledge on the basic mechanisms of the new particle formation process in different environments.

The aim of Horizon 2020 Marie Sklodowska Curie Actions (MSCA) Individual Fellowship project Nano-CAVa is to characterize the sources and concentrations of atmospheric clusters and nano-particles, study their spatial and temporal variability in different environments, and find out how and when the newly formed clusters grow into larger aerosol particles.

METHODS

During the project we have performed both laboratory experiments and field measurements to characterize nano-particles in the atmosphere and processes leading to their formation.

We collected and reviewed field measurements of the concentration of 1-3 nm particles with the Particle Size Magnifier (PSM, Vanhanen et al. 2011) from 9 sites around the world (Kontkanen et al. 2016). This includes the first published long-term (~1 year) time series of 1-3 nm particles from an urban environment (SMEAR III in Helsinki, Finland) and from a rural boreal forest site (SMEAR II in Hyytiälä, Finland). Further measurements with PSM and NAIS (Neutral Cluster and Air Ion Spectrometer) were performed at Jungfraujoch high-alpine research station in Switzerland during summer 2016 (see preliminary results in Fig. 1). Recently, similar measurements were also started at a sub-Arctic site (SMEAR I in Värriö, northern Finland). Measurements with NAIS and (Cl-)API-TOF (Chemical Ionization Atmospheric Pressure Interface Time of Flight mass spectrometer), along with basic aerosol size distribution and composition measurements, were made onboard research ice breaker Akademik Tresnikov during Antarctic Circumnavigation experiment (ACE) and during the passage from southern hemisphere (Cape Town) to northern hemisphere (Bremerhaven) to study the aerosol and trace gas concentrations in clean marine environment.

We performed laboratory experiments on new particle formation in the CLOUD aerosol chamber at CERN (Geneva, Switzerland). By adjusting the chamber conditions (temperature, relative humidity, ionization, UV-light) and trace gas concentrations (O$_3$, SO$_2$, NOx, VOC) in the chamber, we can simulate different kinds of environments and altitudes of the atmosphere. During CLOUD10 (Sep-Dec 2015) and CLOUD11 (Sep-Nov 2016) intensive campaigns we studied particle formation both from biogenic and anthropogenic VOCs (Volatile Organic Compounds), either alone or together with NOx, SO$_2$ and NH$_3$. Additional laboratory experiments have taken place at Paul Scherrer Institute and University of Vienna to characterize and test the nano-particle instrumentation used in CLOUD and during the ACE campaign.
CONCLUSIONS

So far we have concluded from field observations that 1) atmospheric cluster formation is connected to photochemistry (Kontkanen et al. 2017, Jokinen et al. 2017) and 2) the concentrations are mainly driven by the availability of pre-cursor vapours rather than limited by the condensation sink (Kontkanen et al. 2016a; 2017). 3) Sulphuric acid and industrial activities were also identified as potential sources of atmospheric nano-particles (Sarnela et al. 2015, Konkanen et al. 2016a). The on-going analysis of the data from Southern Ocean and Atlantic Ocean will reveal if new particle formation events also happen in marine environment, and, more specifically, if the rapid iodine oxide nucleation process, recently found in Mace Head on the west-coast of Ireland (Sipilä et al. 2016) is limited to coastal environments, or if the process is efficiently producing CCN also above open oceans.

Based on laboratory experiments we have: 1) revealed a new growth mechanism of nano-particles by collisions by acid-base clusters (Lehtipalo et al. 2016, Kontkanen et al. 2016b) and 2) for the first time experimentally quantified the magnitude of enhancement due to ions on the early growth process (Lehtipalo et al. 2016). Furthermore, we have proven 3) that particle formation and early growth process can happen solely from biogenic vapours without involvement of sulphuric acid (Kirkby et al. 2016, Tröstl et al. 2016) and 4) that growth rates exhibit a clear size dependency, explained by the Kelvin effect and the volatility distribution of the organic pre-cursor vapors (Tröstl et al. 2016). Recent efforts have concentrated on estimating the importance of ions in new particle formation process (Wagner et al. 2017), and studying particle formation from a mixture of biogenic and anthropogenic vapours in conditions similar to boreal forest (Lehtipalo et al. 2017).
ACKNOWLEDGEMENTS

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AIRBORNE OBSERVATIONS OF AEROSOL PARTICLES IN LAPLAND

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Keywords: AIRBORNE, CLUSTERS, NUCLEATION, PSM.

INTRODUCTION

Atmospheric new particle formation occurs all over the world, under different environments, in clean areas as well as in polluted big cities, and vertically from the ground level, inside the planetary boundary layer, up to the free troposphere. Here we present preliminary results of aerosol particles from a flight measurement campaign in the lower atmosphere in Finnish Lapland. We were flying over Eastern and Western Lapland. Around the operated area we have supporting observations from the ground-based measurement stations in Värriö and Pallas. By combining the ground-based observations, Cessna airborne observations from ground level up to 3500 meters (a.m.s.l.) and HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) air-mass trajectory analysis, we are able to study vertical and horizontal differences and similarities in aerosol populations. Earlier Väänänen et al., 2013 have compared the particle size distributions between three measurement stations in northern Scandinavia including two stations above.

METHODS

The campaign took place in 11.–25.8.2017 and oriented to Finnish Lapland. Total 20 research flights were flown departing from Kittilä airport. One flight took 3 hours.

The instrumentation on board a small Cessna 172 research aircraft included aerosol instruments, H₂O- and CO₂–gas analyser and devices for basic meteorological parameters (pressure, relative humidity, temperature). Total particle concentration was measured with an ultrafine Condensation Particle Counter (uCPC, model TSI 3776) with 3 nm cut-off size and a PSM A10 (Vanhanen et al., 2011) (with CPC TSI 3010 as a counter) with 1.5 nm cut-off size. The total particle number size distribution was measured with a Scanning Mobility Particle Sizer (SMPS) in the size range of 10–400 nm. For instrumentation, see also Schobesberger et al., 2013 and Väänänen et al., 2016.

The SMEAR (Station for Measuring Ecosystem-Atmospheric Relations) I station is located in Värriö, Salla in Eastern Lapland near to Russian borderline (see Hari et al., 1994) and Pallas, Sammalluntunturi measurement site at the Pallas–Sodankylä GAW (Global AtmosphericWatch) station is located in Western part of Finnish Lapland (see Hatakka et al., 2003). The distance between stations is about 230 km.

The data from the ground stations includes total particle size distributions measured with Differential Mobility Particle Sizer (DMPS) in the size range of 7–500 nm in Pallas and 3–700 nm in Värriö and ion size distributions measured with Air Ion Spectrometer (AIS) in the size range of 0.7–42 nm. During the last part of the campaign the total particle concentrations were measured with PSMs with different cut-off sizes, starting at 1.2 nm at the both stations on the ground. Also meteorological data is available.
One of the campaign days, 15th of August was a clear new particle formation (NPF) event day at ground observation stations (Fig. 1). The event started at 4 nm size around 10 o’clock (UTC+2). It is better seen at Värriö station. Cloudiness was disturbing observations of the first hours of the NPF event in Sammallunturi, Pallas. During the day we conducted a measurement flight to both stations: the morning flight at 7:30-10 o’clock to Pallas area and the evening flight at 16:00-17:30 near to Värriö station (Fig. 2 and 3).

In the early morning, total cluster concentration was quite low, about 200-400 cm⁻³, inside the boundary layer, rising from that during the flight up to 2200 cm⁻³. In the evening flight, the cluster concentration has been in level of 2000 cm⁻³. The cluster concentration was quite homogeneous inside the boundary layer at altitudes of 500 – 2000 m from the mean see level during the measurement day. At the start of event observed at stations, we have not been flying.

![Figure 1. Total particle size distribution measured with DMPS at SMEAR I, Värriö, Salla on 15.8.2017. Flight times are marked with vertical black lines in figure.](image1)

![Figure 2. Cluster (red) and 3–10 nm (blue) particle concentrations inside boundary layer during the two measurement flights on 15.8.2017. Particle concentrations were measured by PSM with 1.5 nm cut-off size, uCPC with 3 nm cut-off size and SMPS with 10 nm cut-off size.](image2)
CONCLUSIONS

The first measurement campaign was performed with a Cessna research aircraft in Finnish Lapland in August 2017. The measured data from the flight setup included the size distribution and total particle concentrations with different cut-off sizes of airborne particles, CO$_2$/H$_2$O gas concentrations and meteorological parameters. Altitudes where we operated were from 300 m up to 3500 m (a.m.s.l), and the airborne measurements are supported by the data from SMEAR I and Pallas-Sodankylä GAW ground observation stations. The preliminary results from the campaign are ready, however, more detailed analysis is needed.

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REFERENCES


APPLYING CAUSAL MODELLING TO SMALL-SCALE WOOD COMBUSTION DATA

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Keywords: combustion aerosol, chamber experiment, atmospheric aging.

INTRODUCTION

Small-scale combustion processes produce a substantial part of anthropogenic aerosol and trace gas emissions. Anthropogenic emissions are shown to have significant effect on global warming and human health. Direct mechanisms between emissions and global warming are not completely known, neither is the transforming of emissions in atmosphere. It is also important to investigate secondary organic aerosol (SOA) formation of emissions and factors affecting SOA in order to obtain better understanding about the overall impact of emissions on atmosphere. SOA has been anticipated to have importance in induction of adverse health effects, but there has been a lack of suitable research methods for proving this assumption (Hallquist et al., 2009).

The goal of this study is to investigate how the aging of combustion emissions in atmospheric conditions affect to adverse health and climatological effects of aerosols. We are aiming to determine important factors of emissions with respect to their atmospheric effects. As a by-product, we will try to develop a quantitative measure of main effects of combustion emissions on climate and human health and the cause-consequence chain of the reactions leading from fresh emission to these adverse effects.

METHODS

The data for our study were collected in chamber experiments, conducted in ILMARI environmental chamber at the University of Eastern Finland (Leskinen et al., 2015) between 3rd and 9th February, 2015. In ILMARI environment, it is possible to investigate the aging of combustion emission in atmospheric-like conditions in a controlled environment.

The dataset includes five experiments where spruce logs were burned in a conventional masonry heater. Emissions were injected into the chamber where the chemical composition if aerosol particles and gas phase, as well as aerosol concentration and size distribution were measured with AMS, PTR-MS, SMPS and several gas analysers.

In the chamber, it is possible to compare night- and daytime aging processes and investigate effect of the major oxidizers: ozone, OH radical and nitrate radical in detail. Three experiments contained both dark and daytime aging and two experiments only daytime aging.

Measured variables and variable relationships are studied with causal model. Causal model includes causal structure and group of equations that represents how values of variables are selected. Causal structure is a directed acyclic graph that defines how each variable is influenced by other variables. (Pearl, 2009)
By using causal model and causal calculus, it is possible to do statistical inference how variables relate to each other and compute how much changing of one variable affects to other variables (Pearl, 2009). Despite the fact that causal models are powerful tools for complex atmospheric measurement data, they have not been used before with these kind of data.

Causal structure have to be determined before estimating parameters of equations. The structure could be determined by using prior knowledge of the investigated phenomenon or by using algorithms that can search variable relationships by using observed structure of variables in data. Algorithms can use e.g. covariance structure of variables to determine relationships between variables.

In this study, both of the above-mentioned methods are applied because exact causal structure of measured variables is not completely known. First, relationships are searched by using data and already implemented algorithms (Wongchokprasitti, 2017). The found relationships are evaluated with the knowledge on known reaction paths so that obvious miss-determinations can be ruled out, lacking, but assumed to be important, effects can be included and their significance tested. After relationships have been determined, we can estimate the effects between variables. Figure 1 shows an example of a possible causal graph between variables given by the automated algorithm. The arrows indicate the suggested pathways of the effects. Note that these pathways are unconfirmed and the figure is only illustrative.

![Illustrative causal graph of variables](image)

Figure 1. Illustrative causal graph of variables. Arrow pointing from variable X to variable Y means that variable X is a cause of variable Y.

**CONCLUSIONS**

Combination of ILMARI research facility and Causal models, which give explicit information about evolvement of emissions, offers a setting for significant scientific innovations and is able to overcome several major limitations of the traditional methods used in air pollution research related to health effects.
ACKNOWLEDGEMENTS

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REFERENCES


EFFECT OF TEMPERATURE ON EVAPORATION OF SECONDARY ORGANIC AEROSOL FROM PHOTOOXIDATION AND OZONOLYSIS OF α-PINENE

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Keywords: temperature, evaporation, secondary organic aerosol, α-pinene

INTRODUCTION

Secondary organic aerosol, referred to as SOA, comprises the majority of atmospheric sub-micron aerosols and strongly determines environmental impacts of aerosol particles in the atmosphere. SOA is formed either via condensation or via nucleation following oxidation of gas-phase trace reactive organic compounds. Various organic species in SOA differ in elemental ratios, chemical structure, viscosity, volatility and other aspects. Complexity arising from the chemical and physical features of SOA is one of the most important challenges in describing the condensation or evaporation of aerosol particles in the atmosphere.

One key aspect to be investigated is the volatility of SOA constituents, which governs their partitioning between gas phase and particulate phase. The Volatility Basis Set (VBS) approach, a widely used approach in describing the aerosol volatility, categorized organic compounds based on their saturation mass concentration (C*) (Donahue et al. 2006). Typically, in conjunction with the equilibrium gas-particle partitioning theory, VBS framework can be used to describe chemical composition both in gas phase and in particle phase. However, previous studies have reported slower SOA evaporation compared to that derived from VBS parametrizations (Vaden et al. 2011, Wilson et al. 2014, Yli-Juuti et al. 2017). It is suggested that this slower SOA evaporation is attributed from particle-phase diffusion limitations arising from the viscosity of particles (Vaden et al. 2011, Wilson et al. 2014), or from a combination of mass transport limitations and chemical reactions in condensed phase, such as oligomer degradation (Roldin et al. 2014, YliJuuti et al. 2017). Recent studies have revealed that molecular diffusion in particles slows down in response to lower temperature, indicating increasing particle viscosity (Price et al. 2015, Bastelberger et al. 2017), while oligomer decomposition becomes more favourable under higher temperature, leading to the formation of smaller and more volatile organic compounds (Hall IV and Johnston 2012, DePalma et al. 2013). Given the importance of these physical and chemical processes on SOA evaporation, investigations on SOA evaporation at low temperature are highly needed. In this work, we study SOA formed in ozonolysis and photooxidation of α-pinene and investigate the evaporation of the particles at relative humidity (RH) ranging from 0% to 80% both at warm temperature (20 °C) and at cold temperature (10 °C).

METHODS

SOA with similar O:C ratio between 0.51 and 0.62 was generated either from photooxidation or from ozonolysis of α-pinene, with a continuous quartz flow tube reactor at room temperature (25 °C). After exiting from the flow tube reactor, SOA went through size selection in two Differential Mobility Analysers (DMA, model 3081, TSI). Then the monodisperse particle sample with mobility diameter 80 nm was either led into the bypass line for direct size measurement or fed into two 100-L Residence Time Chambers (RTC). Both the DMAs, by-pass line, and the RTCs were inside a temperature-controlled room either at 10 °C or at 20 °C. The two DMAs operated in an open-loop sheath flow configuration, which effectively removed the majority of gas phase organic compounds and led to the evaporation of the particles. SOA filling to the RTCs was not stopped until the desired particle number concentration was reached. After this, the voltage of the DMAs was set to 0V, and the RTCs were closed. RH was set to 0%, 20%, 30%, 40% or 80% for both RTCs, and this was controlled by the humidity of sheath flows of DMAs.
Short residence time data points were collected from the bypass measurement with varying tube length, while intermediate and long residence time data were collected from RTCs within the period of SOA filling and with one-hour intervals after SOA filling, respectively. Particle size was monitored with a Scanning Mobility Particle Sizer (SMPS, model 3080, TSI). The elemental composition of particles was measured by a High Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS, Aerodyne Inc.). Setup for SOA evaporation experiments is shown with details in Figure 1.

![Figure 1](image)

**Figure 1.** Schematic diagram of the set-up for evaporation experiments on α-pinene SOA.

**RESULTS AND CONCLUSIONS**

For all the investigated environmental conditions, particle evaporation was faster at 80% RH compared to dry conditions. In addition, as expected, SOA evaporated slower at 10 °C than at 20 °C, which is likely caused by decrease of saturation concentrations with decreasing temperature and potentially also by the increasing particle viscosity and/or by the decreasing rate of oligomer decomposition. At colder temperature, particles generated from α-pinene photooxidation evaporated slower and had larger diameter after staying in the RTCs for several hours, which indicates that more organic compounds remained in the particle phase. Similarly, α-pinene ozonolysis SOA showed a slower evaporation trend at 10 °C compared to that at 20 °C. Interestingly, for SOA that was formed by photooxidation of α-pinene, the difference in evaporated fraction between 20 °C and 10 °C was significant at 20% RH. While the SOA evaporation rate at 20% RH was closer to higher RH cases under warm temperature, under cold temperature it was substantially slower and closer to the dry case. However, the evaporation of ozonolysis α-pinene SOA at 20% RH almost overlapped with that at wet condition both at 20 °C and at 10 °C.

Here, we preliminarily conclude that the during the particle evaporation process, temperature affects saturation vapour pressures as well as diffusion limitations in particle bulk, and possibly impacts the decomposition rate of dimers in the particle. In addition, the observed differences between two SOA types are due to the chemical composition, in spite of their similarity in O:C ratio. The in-depth analysis is on progress and in the future, a kinetic evaporation model will be employed to analyse the potential factors controlling this observed evaporation behaviour in more detail.
Figure 2. Measured evaporation of α-pinene SOA from photooxidation with initial mobility diameter 80 nm as function of residence time under varied relative humidity at 20 °C. The y-axis presents the evaporation factor (EF), i.e. the particle diameter divided by the initial diameter.

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CHARACTERIZATION OF AEROSOL OPTICAL PROPERTIES IN WESTERN SAUDI-ARABIA USING POSITIVE MATRIX FACTORIZATION

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Keywords: aerosol, scattering, absorption, positive matrix factorization

INTRODUCTION

To clearly derive the comprehensive aerosol in situ properties at a rural background area in Saudi Arabia, aerosol measurements station was established to Hada Al Sham, 60 km east from Red Sea and city of Jeddah. Here we introduce observations of the aerosol optical properties, scattering and absorption coefficients, Ångström exponents and single scattering albedo over the measurement period from February 2013 to February 2015. As expected, scattering coefficient was dominated by large particles with low Ångström scattering exponent most probably desert dust. Especially from February to June the Ångström scattering exponent was clearly lower and scattering coefficients higher than total averages because of dust storm season. Positive Matrix Factorization mathematical tool was applied to scattering and absorption coefficients and PM$_{2.5}$ and coarse mode (PM$_{10}$-PM$_{2.5}$) mass concentrations to identify different source characteristics. Three different factors were found each with clearly different properties, anthropogenic, night time and desert dust.

METHODS

Detailed descriptions of the station and the measurement program and methods are given in Lihavainen et al., 2016 and 2017. The measurement station was located at rural background site at Hada Al Sham (21.802° North, 39.729° East, 254 m a.s.l.), figure 1. The site is situated about 60 km east of the coast of the Red Sea and the city of Jeddah with a population of around 3.4 million and 43 km north of city of Mecca with a population of around 1.3 million. In situ data reported here is from February 2013 to February 2015 due to a malfunction in the measurement setup preventing proper observations.

Aerosol scattering coefficient at three wavelengths (450, 525 and 635 nm) were measured with Ecotech Aurora Nephelometer. Aerosol absorption coefficient at seven wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) was measured with Magee Scientific AE31 Aethalometer. The inlet to these instruments had PM10 cut-off nozzle. The sample air was dried with twin diffusion dryer prior entering to the instruments. Measurements and data processing were done according to GAW recommendations.

Other measurements at the station included PM$_{10}$, PM$_{2.5}$, aerosol size distribution from 7 nm to 10 µm, weather parameters (temperature, relative humidity pressure, wind speed and direction) and Aerosol Optical Depth (AOD) with Cimel CE-318 sun photometer as part of AERONET measurement programme (Holben et al., 1998).

Positive matrix factorization (PMF) Receptor model (Paatero and Tapper, 1994), a commonly employed method was used for apportionment of source strength using speciation data. EPA PMF 5.0 program was
applied to scattering and absorption coefficients at three wavelengths, PM$_{2.5}$ and coarse (PM$_{10}$ – PM$_{2.5}$) mode aerosol mass concentration. PMF is a receptor-only, factorization model based on mass conservation which requires no a priori information about factor profiles or time trends. PMF has generally been applied to long-term, low-time-resolution datasets, though there has been a call for greater application of source apportionment techniques to air pollution events to facilitate understanding of specific sources for regulatory purposes (Engel-Cox and Weber, 2007).

CONCLUSIONS

Scattering and absorption coefficients at three wavelengths and PM$_{2.5}$ and the coarse (PM$_{10}$ – PM$_{2.5}$) mode mass concentrations (Lihavainen et al., 2016) were used to identify source characteristics and contributions with PMF analysis. Three scientifically sound factors with clearly different characteristics were found. For simplicity we assume here that the aerosol is more externally mixed, three factors and their combinations.

![Figure 1](image1.png)

Figure 1. On top (a) is diurnal variation of factors 1-3 and at the bottom (b) variation of factors 1-3 as a function of wind direction (WD). Values are calculated over the campaign period. The factor numbering is 1) anthropogenic, 2) BC source and 3) desert dust.

Analysis revealed three clearly different types of sources; 1) anthropogenic, 2) BC source and 3) desert dust. These factors have clearly different seasonal variation. The contribution of desert dust factor was dominating from February to May, whereas the contribution of anthropogenic factor is quite steady over
the whole year. Diurnal variation of contribution of factors is presented in figure 1a and variation of contribution of factors with wind direction in figure 1b. In figures 1a and 1b the average of contribution over the variable is one. We calculated the mass absorption and scattering efficiencies for the factors and they agreed well with earlier observations. Hence, this method could be used to distinguish characteristics of aerosol optical properties from different sources, at least in fairly simple cases.

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REFERENCES


BELOWGROUND HYDRAULIC CONDUCTANCE IN MATURE SCOTS PINE TREES

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Keywords: PINUS SYLVESTRIS, POINT DENDROMETER, SAP FLOW, STOMATAL CONTROL

INTRODUCTION

Understanding tree water use and water balance is important as photosynthetic production and tree growth are limited by the capacity of trees to extract water from the soil and transport it to leaves. Belowground hydraulic conductance \( k_{bg} \) is one of the least understood component of the hydraulic pathway between soil and atmosphere. While \( k_{bg} \) has been measured for smaller plants and tree seedlings of various species in laboratory, it has seldom been measured continuously for mature trees in field conditions (Martínez-Vilalta et al. 2007; McElrone et al. 2007). We studied the dynamics of belowground hydraulic conductance of three mature Scots pine trees in field conditions using continuous xylem diameter change and sap flow measurements over several full growing seasons. Our aim was 1) to analyze how soil temperature and soil water content is linked to \( k_{bg} \), and 2) to analyze how stomatal conductance \( (g_s) \) is affected by \( k_{bg} \). \( k_{bg} \) was calculated as the ratio of daily maximum sap flow rate to the difference between stem and soil water potential estimated from daily diameter variations of xylem measured with point dendrometers.

METHODS

We measured three Scots pine trees in a boreal, evergreen coniferous forest at SMEAR II in Hyytiälä: tree 1 in year 2016, trees 1 and 2 in year 2015, and tree 3 in year 2013. Belowground hydraulic conductance was calculated as the ratio of daily maximum of sapwood-specific flow rate to the difference between daily maximum and daily minimum of xylem diameter. Sap flow density was measured with constant heat dissipation sensor. The water potential difference between the stem base and the soil was derived from xylem diameter measurements at breast height; stem water potential is assumed to be proportional to xylem diameter (e.g. Irvine and Grace 1997) and soil water potential linearly proportional to the highest xylem diameter encountered during the night, (Martínez-Vilalta et al. 2007). Xylem diameter was measured continuously with linear displacement transducer point dendrometers. In addition, photosynthetic active radiation (PAR), vapor pressure deficit (VPD) in 16 meters, soil temperature and relative water content in B1 horizon (9-14 cm depth) were measured. \( K_{bg} \) was normalized with the maximum value for each tree for each year to be able to compare the dynamics of \( K_{bg} \) between different individuals and years. Stomatal conductance was calculated as the ratio of daily maximum sapwood-specific sap flow and daily maximum vapor pressure deficit.

RESULTS

In spring, soil temperature and belowground conductance increase and soil water content decrease towards the summer (Fig. 1). In autumn, soil temperature decreases again and soil water content increases, while \( k_{bg} \) decreases (Fig. 1). \( k_{bg} \) increased with increasing soil temperature during all seasons, but the increase was clearly higher in spring than in summer or autumn (Fig. 2). \( k_{bg} \) increased also with increasing soil water content, but only if soil temperature was high enough. Stomatal conductance was positively correlated with \( k_{bg} \).
Figure 1. Time series of normalized belowground hydraulic conductance ($k_{bg}$), soil temperature and relative soil water content in and example year 2013.

Figure 2. Normalized belowground hydraulic conductance ($k_{bg}$) plotted against soil temperature in spring, summer and autumn. Linear fits are drawn for each season.

CONCLUSIONS

The method of estimating belowground hydraulic conductance from simultaneous field measurements of sap flow and xylem diameter change gave reasonable results over the period chosen in terms of consistency of the time series of $k_{bg}$ over the season between years and trees, and dependency of $k_{bg}$ on soil temperature and soil water content. We showed that belowground hydraulic conductance was connected to soil temperature and soil water content, but the effect of soil water content on $k_{bg}$ was overruled by soil temperature in spring and autumn. Belowground hydraulic conductance is increasing with increasing temperature likely due to decreasing viscosity and increasing aquaporin activity. Aquaporins enable rapid water flow through cell membranes in plants, and their activity is the higher the higher the temperature until an optimum is reached (Murai-Hatano et al. 2008). Also new root tips and mycorrhizas grow in spring when soil temperature increases above a certain threshold temperature, and the number of mycorrhizas per root length have been shown to increase with increasing soil temperature (Domisch et al. 2002) thus increasing $k_{bg}$. Belowground hydraulic conductance was also strongly linked to stomatal conductance, especially when the soil was cold.
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REFERENCES


SIMULATING CANOPY SCALE SOLAR-INDUCED CHLOROPHYLL FLUORESCENCE IN A REALISTIC BOREAL FOREST SCENE

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KEY WORDS: CHLOROPHYLL FLUORESCENCE, UPSCALING, DART, 3D SCENE, FOREST

INTRODUCTION

Solar induced chlorophyll a fluorescence (SIF) is an excellent proxy of photosynthesis at multiple scales. Although there is a substantial body of evidence linking fluorescence to photosynthesis for leaves, these between SIF and photosynthesis at the leaf level cannot be directly utilised at the canopy scale, because of the effect of canopy structure (Porcar-Castell et al., 2014; Migliavacca et al., 2017). Recently, 3D radiative transfer codes have been developed that incorporate SIF, and such codes can be used to assess the impact of realistic forest structure on fluorescence. Here we present a combined SIF modelling framework which combines the 3-D radiative transfer model DART, and the 3-D object model BLENDER. Our aim was to better understand the impact of forest structural variation on SIF, for a realistic boreal forest scene.

METHODS

Our study used the Discrete Anisotropic Radiative Transfer (DART) (Gastellu-Etchegorry et al., 2017), a comprehensive physically based 3-D RT model, which is designed to numerically solve the radiative transfer problem in complex and heterogeneous 3-D landscapes, e.g. forest scenes. Embedded within the DART model is Fluspect RT model (Van et al., 2011), a leaf scale radiative transfer model capable of simulating chlorophyll a fluorescence.

We used Blender (Allan Brito, 2008), a free and open source 3D modelling software, to create realistic 3-D birch trees based on forest survey data collected at our measurement sites, close to Hyytiälä forestry.
field station, Finland. The 3-D trees in the forest scene were modelled with a set height of 17.5 m, and diameter of crown of 2.8 m; these were mean values from our survey data. For the leaf inclination angle we used a spherical distribution and ellipsoid was used to model the crown shape. Below our trees, we implemented a 3-D grass layer (10 centimeter in thickness, LAI=1) as a simplification of the effect of multiple canopy layers found at our measurement site.

The measurement site was a stand (20 m in diameter) mainly consisting of Silver birch (Betula pendula Roth) trees, located close the Station for Measuring Ecosystem-Atmosphere Relations II (SMEAR II), Finland. We surveyed the following variables for each tree in the 20 m diameter: coordinates, tree height, crown height and DBH (Diameter at Breast Height). We used this data to parametrize the 3D model shown in Figure 1. We also measured ground and bark reflectance in the field using a FieldSpec-HH spectrometer (ASD, Panalytical Devices, Ltd) with a sampling interval of 1.6 nm and spectral resolution of 3.5 nm. In the laboratory we measured leaf reflectance and transmission using an integrating sphere (Adapa Sphere, LabSphere, North Sutton, NH, USA) coupled to the above described FieldSpec-HH spectrometer.

RESULTS AND CONCLUSIONS

Figure 2 shows the simulated SIF image at 740nm. In this scene we used 0.5 m spatial resolution and 1 nm spectral resolution. Simulated full-spectrum canopy reflectance radiance and SIF are shown in Figure 3, this result can be used top assessed the overall role of forest structure on the re-absorption of red fluorescence and, to a lesser extent, far red photons. By including a fluorescent background we also take the first steps towards assessing the role of multiple canopy layers in a complex scene. Such an assessment is necessary in the boreal forests, where there after often 2 or more ‘layers’ contributing to above canopy optical signals.

Our next steps are to validate our simulations using hyperspectral data measured from a drone platform (Honkavaara et al., 2016) equipped with a Piccolo Doppio system (Mac-Arthur et al., 2014). This data has been collected over spring and summer 2017 as part of the FAST 2017 campaign (Fluorescence Across Space and Time). The Piccolo Doppio uses a QePro Ocean Optics Spectrometer for retrieval of canopy SIF in the oxygen B and A bands and an Ocean Optics Flame for visible and near infrared reflectance.

![Figure 1. Forest 3-D scene: (a) Nadir view. (b) Side view](image)
Figure 2. SIF image at 740nm in nadir view (Unit: W/m^2/µm/sr)

Figure 3. Canopy reflectance and SIF spectrum

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INTRODUCTION

Aerosol particles have a direct impact on the climate by scattering and absorbing the radiation from the sun. The optical properties of aerosol particles describe how much the particles scatter and absorb light on different wavelengths. The radiative forcing related to the aerosol particles has still large uncertainties and especially determining the warming effect of the absorbing particles has turned out to be a challenging task (Myhre et al., 2013).

Usually, the absorption of aerosol particles is measured by filter-based methods. However, measuring the absorption by collecting the particles on a filter leads to systematic errors, which are caused by the interactions between the filter material and the particles. The filter material consist of quartz fibers, which also scatter light. The optical path of the light beam through the filter gets longer if the light is scattered on the way. Longer path leads to a higher probability for the light to be absorbed on the particles and thus the measured apparent absorption coefficient ($\sigma_{\text{ATN}}$) seems higher than the real absorption coefficient ($\sigma_{\text{abs}}$). This multiple scattering by the filter is corrected with a multiple scattering correction factor ($C_{\text{ref}}$). Also the particles that are suspended on the filter cause an error to the measurements since the particles are collected on a filter, the attenuation (ATN) in the filter is increasing. The more there are absorbing particles in the filter, the more light gets absorbed and thus the optical path of the light beam in the filter is shorter. The higher the filter attenuation is, the lower the $\sigma_{\text{ATN}}$ is compared to the real $\sigma_{\text{abs}}$. The error caused by the increasing ATN is corrected with a filter loading correction (R) which depends on the ATN. To get the $\sigma_{\text{abs}}$ from the $\sigma_{\text{ATN}}$ measured by the aethalometer, the $\sigma_{\text{ATN}}$ needs to be corrected with the $C_{\text{ref}}$ and R(ATN).

$$\sigma_{\text{abs}} = \frac{\sigma_{\text{ATN}}}{C_{\text{ref}} R(\text{ATN})}$$

There are several different filter loading correction algorithms developed by Weingartner et al., (2003); Arnott et al., (2005); Virkkula et al., (2007) and Collaud Coen et al., (2010) which were used also in this study.

METHODS

The measurements presented in this study were conducted at the SMEAR II station during 2013 - 2016. The SMEAR II station is located in Hyytiälä, Southern Finland (61°51’N, 24°17’E) and the station represents conditions in a boreal forest. In this study, the $C_{\text{ref}}$ was determined at the SMEAR II station by comparing the $\sigma_{\text{abs}}$ measurements by the Aethalometer (Magee Scientific model AE-31) and the Multi-Angle Absorption Photometer (MAAP, Thermo model 5012) with each other. In this study the MAAP was used as the reference instrument. The scattering coefficient ($\sigma_{\text{scat}}$), which is needed in some of the correction algorithms, was measured with an integrating nephelometer (TSI model 3563).
The $C_{\text{ref}}$ is determined by correcting the $\sigma_{\text{ATN}}$ measured by the Aethalometer with the $R(\text{ATN})$ and comparing the results with the $\sigma_{\text{abs,ref}}$ measured by the MAAP.

$$C_{\text{ref}} = \frac{\sigma_{\text{ATN}}}{R(\text{ATN})\sigma_{\text{abs,ref}}}$$

The Aethalometer measures the $\sigma_{\text{ATN}}$ at seven wavelengths (370, 470, 520, 590, 660, 880 and 950 nm) as MAAP uses just one wavelength (637 nm). The Aethalometer data measured at the 660 nm was used in the comparison since it’s the closest wavelength to 637 nm.

CONCLUSIONS

The median values, the standard deviation and the seasonal variation of the $C_{\text{ref}}$ for the different correction algorithms are presented in the figure 1. In theory, the $C_{\text{ref}}$ should be a constant since it should only depend on the filter. However, at the SMEAR II station there was a clear seasonal variation for the $C_{\text{ref}}$ for different algorithms as presented in the figure 1. The $C_{\text{ref}}$ was higher than the median during the summer and fall (June – October) and lower than the median during the winter and spring (Jan – April).

![Figure 1. The seasonal variation the $C_{\text{ref}}$. Edges of a box represent the 25th and 75th percentiles, the line in middle is the median and the whiskers represent the 10th and 90th percentiles.](image)

The reason for the variation was investigated by comparing the $C_{\text{ref}}$ values against different properties as presented in the figure 2. If the data is not corrected for the filter loading, the $C_{\text{ref}}$ had a dependency on the ATN, but if the correction is made there’s no dependency. For the single scattering albedo ($\omega$), the only correction algorithm which correlates with the $C_{\text{ref}}$ was the Collaud Coen algorithm. In the algorithm, the loading correction depends on the $\omega$, which explains the dependency between the $C_{\text{ref}}$ and $\omega$. For the backscattering fraction ($b$) there’s no $C_{\text{ref}}$ dependency for any of the correction algorithms. Even though these optical properties ($\omega$ and $b$) also have a strong seasonal variation, they don’t seem to affect the $C_{\text{ref}}$.

The only property, which correlates with the $C_{\text{ref}}$ for each of the correction algorithms, was the relative humidity (RH) of the air. The higher the RH is (in the lab room temperature), the higher is the $C_{\text{ref}}$ also.
Even though the RH is below 100 %, the solid aerosol particles may still take up water and form a liquid droplet. The droplets may stay in the liquid state if the sample air is not dried enough. When the liquid droplets collide into the filter, the filter takes up the moisture of the droplet. If the filter takes up water, the optical properties of the filter fibres change which may therefore cause the increase in the $C_{\text{ref}}$ as well.

![Boxplots of the dependency of $C_{\text{ref}}$ on the ATN, $\omega$, $b$ and RH. The explanation to the boxplots is the same as in the figure 1.](image)

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**REFERENCES**


INTRODUCTION

The development seamless/ on-line integrated meteorology-chemistry-aerosols modelling system such as the Enviro-HIRLAM (Environment – High Resolution Limited Area Model) is expected to be able to handle and study some of major existing processes and interactions, which is difficult to investigate using the off-line modelling approach. Following Jacobson et al. (2007) and Zhang (2008), among these processes and interactions there are the following. At first, the direct effect - radiative effect of chemical species such as ozone and aerosols in the atmosphere via absorption and scattering. At second, the semi-direct effect - effect of aerosols and clouds on photolysis rates via modifying actinic fluxes and temperature. At third, the semi-direct effect - effect of aerosols on boundary layer meteorology via changing meteorological variables and atmospheric stability. At fourth, the first and second indirect effects - effect of aerosols on cloud formation and reflectance via aerosol activation, droplet and ice core nucleation, autoconversion, and collection. And, at forth, the indirect effects - effect of aerosols on precipitation by affecting clouds and water vapour. These processes and interactions are important in studies for weather, climate, air quality, ecosystems, etc. Aerosols, being an integral part of the atmosphere, play important role in the environmental conditions behaviour. Depending on origin, chemical composition, lifetime, size, shape, optical properties, etc. aerosols can cause multiple complex effects in the atmosphere at various temporal and spatial scales (Kulmala et al., 2009; Calvoa et al., 2012). The focus of the Pan-Eurasian Experiment (PEEX; https://www.atm.helsinki.fi/peex) programme is on the Northern Eurasia, e.g. large territories of the Arctic and boreal regions as well as China. PEEX is a long-term interdisciplinary climate change, air quality, environment and research infrastructure programme, and the PEEX-Modelling-Platform (PEEX-MP) is the part of this infrastructure (among observations, monitoring and data systems). It has utilised more than 30 models, which are running on different spatial-temporal scales and resolutions as well as geographical domains in focus. These models are used as research tools capable to provide insights and valuable output for assessment studies for environment and population. One of these research models is the Enviro-HIRLAM. It has been applied in both the research (in majority of EU and NordForsk funded projects) and recently (as part of the FP7 EU MarcoPolo project) the operational modes as well as at different scales – regional, sub-regional, urban (and hemispheric; in NordForsk CarboNord project). It should be mentioned, that the seamless approach, when modelling of both meteorology and atmospheric composition is done simultaneously (at time and space), will provide additional value for the PEEX related studies, and especially for the aerosols-clouds-radiation-etc. interactions and feedbacks.

In summer of 2017, at UHEL the Enviro-HIRLAM system was installed, setup and tested for several case studies (as short-term runs) at the CSC supercomputer CRAY-XC40. It has been also listed to be used in
METHODS AND RESULTS

Enviro-HIRLAM Model: The Environment – HIgh Resolution Limited Area Model (Enviro-HIRLAM) is developed as a fully online integrated numerical weather prediction (NWP) and atmospheric chemical transport (ACT) model for research and forecasting of joint meteorological, chemical and biological weather at multi-scales (Baklanov et al., 2017). The NWP part developed by HIRLAM consortium (Unden et al., 2002) is used for operational weather forecasting. The Enviro-components were developed in collaboration with the Universities from different countries (Korsholm, 2009; Baklanov et al., 2008, 2010, 2017; Nuterman et al., 2013, 2015; Mahura et al., 2015, 2017). The Enviro- consists (see all references in Baklanov et al., 2017) modules for gas-phase chemistry CBMZ and aerosol microphysics M7, which includes sulfate, mineral dust, sea-salt, black and organic carbon. There are also modules of urbanization (anthropogenic heat flux and roughness, building effect parameterisation, and others) for land surface scheme, natural and anthropogenic emissions, nucleation, coagulation, condensation, dry and wet deposition, and sedimentation of aerosols. The improved Savijarvi radiation scheme takes into account explicitly for aerosol radiation interactions for 10 aerosol subtypes. The aerosol activation scheme was also implemented in STRACO condensation-convection scheme. The nucleation is dependent on aerosol properties and the ice-phase processes are reformulated in terms of classical nucleation theory.

As the modelling system runs in a downscaling chain, for the outer model domain (run at low resolution) the initial and boundary conditions for meteorology and atmospheric conditions are taken from ECMWF. The vertical levels vary between 40-60. The finest horizontal resolution is about 1.5 km. The model can be run in both research and operational modes. Emissions include anthropogenic, biogenic, and natural; and these are pre-processed. Different parts of the model were evaluated versus ETEX-1 experiment, Chernobyl accident, Paris summer/winter campaigns, etc. At urban scales, the model was tested (FPs FUMAPEX, MEGAPOLI, TRANSPHORM, PEGASOS, MACC, MarcoPolo projects) for several metropolitan areas such as for example: Copenhagen (Denmark), Paris (France), Rotterdam (The Netherlands), Vilnius (Lithuania), Bilbao (Spain), St. Petersburg (Russia), Shanghai (China). Several examples of the Enviro-HIRLAM model applicability are shown below (Mahura et al., 2015, 2017).

FP7 EU MEGAPOLI: the Enviro-HIRLAM model at high resolution of 2+ km was used to study variability of multiple meteorological parameters including the air temperature at 2m on a diurnal cycle for Paris (France). The difference between the control/ reference and modified/ urbanized runs was studied, and these were found to be larger during nighttime – early morning hours. When the urban effects are included, these differences are more pronounced (effect of the urban heat island). It clearly underlines that the Paris metropolitan area is significantly warmer than the surrounding rural areas. Under the low wind conditions and with additional increases in anthropogenic heat fluxes (AHF) the impact of the city (or a so-called “foot-print”) can be extended farther (in south-eastern as dominating wind direction) as well as expanded in other directions (Fig. 1a). E.g. it leads to increasing the city’s heat signature and bringing a potential of urban influence for a distance of more than a 100 km away. The temperature differences between urban vs. rural areas became more evident, and can reach more than 5°C (at 250 W/m²) at night on a summer day. The differences is also observed for chemical patterns, as shown on example of ozone (Fig. 1bc). Moreover, for both meteorological and chemical patterns these differences are also seen above the city and surroundings at several model levels (within the boundary layer), although such influence is decreasing with the height.

NordForsk CarboNord: the model was adapted, setup and run at resolution of 15 km for months of Jan and Jul-Aug 2010 as the reference run as well as the runs with direct, indirect and both combined aerosol
effects. The geographical domain covering selected Arctic and boreal regions is of interest for PEEX. The effects of aerosols on meteorology are analysed on a regional scale (an example of statistical evaluation is shown in Fig. 2).

**FP7 EU MarcoPolo**: the model was adapted, tested and setup for China with downscaling operational service as forecasting performed at resolutions of 15, 5 and 2.5 km (for the Shanghai metropolitan area), which is also the area of the PEEX programme research interests. The model is used to study formation and development of meteorological and chemical (with focus on aerosols) fields on regional-subregional-urban scales for the larger part of the most populated territories of China.

**Figure 1**: (a) Diurnal cycle variability of the difference fields for air temperature at 2m (in deg C) with changing anthropogenic heat fluxes (100, 150, 200, and 250 W/m²) on 4 Jul 2009 at 06 and 24 UTCs; & (b,c) Ozone concentration (in ppb) for the control vs. urbanized runs at 21 UTCs on 4 Jul 2009.

**Figure 2**: January 2010: Averaged spatial distribution of the maximum PM2.5 concentration field at (a) 00 UTC and (b) 12 UTC for the month of Jan 2010; & (c) Daily variability of the average, minimum, median, and standard deviation for PM2.5 concentration for the CarboNord domain /based on Enviro-HIRLAM model run with direct aerosol effects included/.

Paris metropolitan area (France)
(Enviro-HIRLAM: urban vs. control runs)
Forecasts as a service are available at: http://www.marcopolopanda.eu/products/regional-air-quality-forecasts/enviro-hirlam. Such service (as set of models runs twice per day at 00 & 12 UTCs for 48 h forecast length) provides forecasts for particulate matter PM10 and PM2.5, air temperature, relative humidity, wind speed and direction, and mean sea level pressure. Simultaneous meteorological output can be used conveniently for better interpretation of air quality results (see example in Fig. 3).

CONCLUDING REMARKS

The Enviro-HIRLAM, being as one the PEEX-MP models, is planned to be further continued developed at UHEL (CSC project – “Enviro-HIRLAM seamless modelling of meteorology-chemistry-aerosols interactions and feedbacks on multi-scales”) and applied for different research tasks according to the PEEX Science Plan (PEEX, 2015) and research proposals. The emphasis is on evaluation and testing of the seamless/online integrated approach for in-depth sensitivity analyses of mechanisms, relationships, feedbacks, interactions, etc. between chemistry-aerosols and meteorology in a changing climate. In particular, the Enviro-HIRLAM can be applied for studies on: feedbacks of aerosols and chemistry on formation and development of various meteorological variables; effects of various feedback mechanisms on aerosols and cloud formation and radiative forcing on urban-regional scales; boundary layer parameterizations; urbanization processes impact on changes in urban weather and climate on urban-subregional-regional scales; providing input to assessments for human and environment; transboundary atmospheric pollution and their local impacts; improving prediction of extreme weather events; integration modelling results into GIS environment for further risk/vulnerability/consequences/etc. estimation, and others.

ACKNOWLEDGEMENTS

Thanks to the Centre for Scientific Computing (CSC; https://www.csc.fi/csc) for technical support and advice. The CRAY-XT5/ XC-30 supercomputing facilities (at DMI) were used as part of the recently completed research projects; and CRAY-XC40 was used at UHEL as part of the CSC project. The ECMWF boundary conditions, meteorological and air quality observations/datasets were used for application, validation and verification of the model in the research and operational modes. The examples of research results presented here were funded by the EU FP7 MEGAPOLI (Grant Agreement Number 212520; http://megapoli.info) and MarcoPolo (Grant Agreement Number 606953; http://www.marcopolopanda.eu) projects. The research is also supported through the NordForsk funding of the CRAICC-PEEX (2014-2015) & -CRUCIAL (2016-2017) and CarboNord (2014-2017) projects. These were coordinated by the Finnish partners (UHEL and Finnish Meteorological Institute), and these are linked with the PEEX (https://www.atm.helsinki.fi/peex) programme tasks.

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REFERENCES


NUCLEATION AND AEROSOL SIZE DISTRIBUTION IN EC-EARTH3

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Keywords: Earth System Model, EC-Earth, nucleation.

We have developed the global Earth System Model EC-Earth in terms of nucleation and subsequent growth. The presented nucleation mechanisms will be included in Coupled Model Intercomparison Project Phase 6 (CMIP6) experiments, specifically the AerChemMIP experiments focusing on aerosols, chemistry and climate interactions.

The aerosols and chemistry in EC-Earth are included in the TM5 transport model. Furthermore, the aerosols are described with seven log-normal modes. Modal approaches to describe aerosol size distribution can not accurately describe the growth of nucleated particles. Growth is implemented by allowing condensation (sulfuric acid and organics) to nucleation mode and moving the tail \((d_p > 10 \text{ nm})\) of log-normal mode to Aitken mode. Modal scheme will benefit if nucleated particles are not implemented as < 2 nm clusters, but instead at a larger diameter (3–10 nm).

Atmospheric nucleation can occur via several pathways, depending on conditions (T, RH) and available vapours. In EC-Earth3-AerChem, we have chosen Vehkamäki et al. (2002) scheme for binary sulfuric acid–water nucleation (mostly active in free troposphere and lower stratosphere) and a semi-empirical boundary-layer (BL) nucleation parameterization.

The nucleation parameterizations estimate nucleation at different diameters, hence the total nucleation rate needs additional quantification. Before implementing to M7 nucleation mode, nucleation rate is converted to formation rate of a larger diameter. We have implemented two optional BL nucleation schemes in EC-Earth3-AerChem, based on Paasonen et al. (2010)

\[
J_2 = 11 \times 10^{-14} \times [H_2SO_4] \times [ORG]
\]  

and Riccobono et al. (2014)

\[
J_{1,7} = 3.27 \times 10^{-21} \times [H_2SO_4]^2 \times [ORG]
\]

As shown above, the two BL nucleation schemes estimate nucleation rate at different diameters (1.7 and 2 nm), and additionally the critical cluster size in Vehkamäki et al. (2002) is parameterized. Fig. 1 describes how we have implemented parallel mechanisms in EC-Earth3-AerChem. First, binary sulfuric acid–water nucleation results in a nucleation rate at a parameterized diameter, usually between 0.3 and 1 nm. This is converted to a formation rate of particles at the diameter of chosen BL nucleation mechanism (1.7 nm for Riccobono et al. (2014) and 2.0 nm for Paasonen et al. (2010)). At this point, we have two formation rates at a known diameter, and these rates are summed up to a total formation rate. However, this diameter is still too small to be included in M7 modal aerosol scheme. Hence, we convert this to a prescribed formation rate diameter \((d_{\text{form}}, \text{usually 5 nm})\). Finally, the total formation rate is given to the M7 module. All conversions between formation rates at different diameters are done with Kerminen and Kulmala (2002) parameterization, with condensation sink and growth rates based on simulated quantities.
Binary sulfuric acid-water nucleation produces a peak concentration at 200 hPa (Fig. 2). The parameter for formation rate diameter \(d_{\text{form}}\) defines the amount of nucleated particles which remain in nucleation mode and which are immediately transferred to Aitken mode (red lines, solid vs. dashed). Increasing nucleation coefficient by one magnitude increased Aitken mode concentrations from 300 to 400 \(\text{cm}^{-3}\) (blue lines).

Figure 2: Vertical distribution of Aitken mode particle concentrations with no nucleation (black) and with several assumptions on BL nucleation mechanism: the diameter in the legend refers to the \(d_{\text{form}}\) diameter, and the Riccobono simulation is complemented with a sensitivity simulation with increased nucleation rate coefficient.

The implemented boundary layer nucleation mechanisms are based on both sulfuric acid and organic vapours - both are needed for nucleation. The parallel binary nucleation involves only sulfuric acid and water, but produces nucleation mostly at high altitudes and cold environments. Hence, the nucleation has a strong sea-land contrast (Fig. 3).

The above implementation of nucleation has been evaluated against several station observations. The two parallel nucleation mechanisms can reproduce the overall seasonal variability in nucleation, as well as diurnal dynamics of the nucleation process. However, the growth of nucleated particles from 10–20 nm to CCN sizes remains generally too low, which is a common issue in current global models. While the model can be missing certain precursors or chemical processes leading to aerosol growth, also the modal aerosol description poses a problem for growth from nucleation to CCN sizes.
Figure 3: Increase ($cm^{-3}$) in N10 ($d_p > 10nm$) due to nucleation (using Riccobono et al. (2014)).

REFERENCES


PERFORMANCE OF MARGA INSTRUMENT IN AMMONIA MEASUREMENTS

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Keywords: ammonia, ammonium, online ion chromatograph.

INTRODUCTION

MARGA (Monitor for AeRosol and Gases in ambient Air) is on an online ion chromatograph which can be used for measuring gas phase concentrations of ammonia and acidic gases, as well as the concentrations of ammonium and other inorganic ions in particulate matter with one-hour time resolution. MARGA instrument has been previously used for measuring ammonia at SMEAR stations in Helsinki and in Hyytiälä, where ammonia concentrations are often below the detection limits of commercial ammonia monitors (in Hyytiälä normally below 0.5 µg/m³ even during the summer time)(Makkonen et al. 2014). In August 2016 MARGA was taken to the ammonia field inter-comparison arranged as a part of MetNH₃-project (metrology for ammonia in ambient air, Joint Research Project (JRP) ENV55, 2014-2017 under the European Metrology Research Project EMRP, http://www.metnh3.eu/typo3/index.php?id=30). Also in this comparison MARGA proved to work well with small concentrations. In this paper we discuss possible artifacts appearing at higher ammonia concentrations.

METHODS

In MARGA instrument water soluble gases are absorbed in a wet rotating denuder (WRD) and particles pass through the denuder to a steam jet aerosol collector (SJAC). Water samples from the WRD and SJAC are collected in two sets syringes filling in turn and injected into an anion and cation ion chromatograph (IC) after adding the internal standard (LiBr). In this study we expected moderate ion concentrations and after the fertilization high ammonia concentrations, therefore we used normal IC loops instead of concentration columns. The instrument is described in more detail in earlier papers (ten Brink et al., 2007, Makkonen et al., 2012).

RESULTS AND DISCUSSION

The MetNH₃-project ammonia inter-comparison was held at an intensively managed grassland in South-Eastern Scotland. In this comparison the hourly ammonia concentrations measured by MARGA were varying from about 0.3 µg/m³ (0.4 ppb) up to 47 µg/m³ (64 ppb) (average 5 µg/m³). The ammonia concentration increased after the fertilization at the measurement site on the 24-25 August, 2016. At midnight, simultaneously with ammonia the ammonium concentration increased up to 3.5 µg/m³. However, the sulfate and nitrate concentrations did not increase with ammonium, but later on the early morning hours.

In an earlier MARGA study in Hyytiälä we noticed that while using a cation IC loop instead of the concentration column, cation concentrations (especially Mg²⁺ and Ca²⁺) were overestimated (Makkonen et al. 2014). When we calculated the ion sums in this study, we saw that the amount of cations was larger most of the time showing that the aerosol is basic, but the excess of cations was much larger during the high ammonia
concentration. Therefore, we assumed that a part of ammonia was passed through the WRD to the SJAC. To estimate the amount of ammonia not diffused in the denuder we calculated first the average excess of cations \( \bar{S}_d \) during days before and after the elevated ammonia concentration, when the ionic ratio of ammonium to the sum of nitrate and sulfate was close to unity.

\[
\bar{S}_d = \frac{\sum_{i=1}^{n} (S_{\text{cations},i} - S_{\text{anions},i})}{n}
\]

After that we calculated the amount of excess ammonium, which was the amount of ammonia not caught by the denuder:

\[
S_{\text{NH}_4\text{excess,i}} = (S_{\text{cations},i} - S_{\text{anions},i}) - \bar{S}_d
\]

Finally, we got the corrected ammonia and ammonium concentrations (Fig. 1). During the high ammonia concentrations about 3-8 % of ammonia was not diffused in the denuder but passed through to the SJAC instead, and was measured as ammonium. Using these corrected ammonia and ammonium concentration, maximum values for ammonia and ammonium were 49 µg/m³ (69 ppb) and 3 µg/m³, respectively.

An additional laboratory test was performed to ensure that the elevated ammonia concentration was not caused by the possible memory effect in the cation ion chromatograph, where the gas samples from the denuder and aerosol samples from the SJAC were injected in turn. A strong ammonium solution (100 ppb as ammonia) was passed through the denuder for several hours in the laboratory. Despite of this, the ammonium concentration in SJAC stayed at the blank level. Later an elevated ammonia concentration was produced by using a permeation tube. Unfortunately we were not able to produce concentrations higher than 8 ppb. In this test ammonium concentration in SJAC did not rise, but stayed at the blank level. In conclusion, memory effect in the ion chromatograph caused by ammonia was not detected in this test.

Figure 1. MARGA ammonia and ammonium concentrations 20 August -24 August, 2016.
The reaction time of MARGA was studied in the same test. After the concentration was stabilized during the nighttime at 8 ppb, the permeation tube was rapidly detached and replaced by a HEPA-filter and an oxalic acid impregnated filter (to remove ammonia) were attached. It took two hours before the ammonia concentration was at the blank level. This indicates that the MARGA reaction time is a bit slow in the case concentrations are changing rapidly.

CONCLUSION

In this study we found that during high ammonia concentration about 3-8 % of ammonia was not collected in the denuder, but it was passed to the steam jet aerosol collector and analyzed as ammonium. The MARGA results should be considered critically during episodes with high concentrations, because it is likely that the capacity of the denuder may be overloaded and all the gas molecules are not able to diffuse in the denuder and may be considered as their aerosol counter-ion.

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REFERENCES


USING GAUSSIAN MIXTURE MODELLING IN TARGET CLASSIFICATION WITH
DOPPLER WIND LIDAR

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Keywords: Doppler, lidar.

INTRODUCTION

Reliable cloud masking and discrimination of precipitation from aerosols is essential for many lidar applications (e.g. Harvey et al. 2013). For lidars operating in the near infra-red region, especially the distinction between precipitation and aerosol signal has been a major difficulty and has required a combination of lidar and a cloud radar (O’Connor et al. 2005). We have studied using Gaussian mixture modelling in target classification with Doppler lidar which allows probability based discrimination between clouds, aerosol, and precipitation by using the combination of variance in the signal-to-noise ratio \(\sigma^2_{\text{SNR}}/\text{SNR}\) and vertical velocity \((w)\).

METHODS

The Halo Photonics Streamline scanning Doppler wind lidar operates in the 1.5 \(\mu\)m spectral region (Pearson et al., 2009). The lowest height Halo lidar is capable of measuring in the vertically pointing mode is 105 m, and it can measure up to 9600 m with 30 meter vertical resolution. Halo lidar provides profiles of SNR, which can be used to calculate attenuated backscatter coefficients \((\beta)\) if the telescope function is known (Hirsikko et al. 2014). It also provides \(w\) profiles with resolution of 0.0382 m s\(^{-1}\) and can measure velocities between approx. -19 to 19 m s\(^{-1}\) in the vertically pointing measurement mode. This study use the \(\sigma^2_{\text{SNR}}/\text{SNR}\), i.e. the variance in the SNR normalized with the SNR itself, and the \(w\). It is assumed that the different targets follow a 2-D Gaussian distributions in the \(\sigma^2_{\text{SNR}}-w\) domain, and thus can be distinguished by clustering with Gaussian mixture modelling.

CONCLUSIONS

This study indicates that clustering and Gaussian mixture modelling can be used in target classification, which would provide a probability based method to reliably distinguish between clouds, aerosols, and precipitation in lidar measurements.

Figure 1. Gaussian mixture modelling results where the parts of the signal which can be reliably associated with either aerosol (red and green) or cloud signal (blue) are illustrated with coloured areas.
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REFERENCES


AEROSOL PARTICLES (0.3-10 µm) INSIDE A WORKSHOP AREA- EMISSION RATE AND DEPOSITED DOSE

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Keywords: indoor air quality, emission rate, deposited dose, educational workshop

INTRODUCTION

People are exposed to particulate matter indoors and outdoors. It has been evidenced that exposure to particulate matter (and more specifically on PM₁₀ and PM₂.₅) is strongly associated with adverse health effects such as asthma, cardiovascular disease, pulmonary inflammation and even lung cancer (Brunekreef and Frosberg, 2005; Pope et al., 2006; Hussein et al., 2015a).

Up until now, most of the researches have focused on measuring particle mass and particle number concentration of coarse and fine particles, respectively (Tran et al., 2012; Voliotis et al., 2014; Slezakova et al., 2015). Therefore, the main purpose of this work is to study, report and illustrate the particle number concentration of micron (1-10 µm) and the particle mass concentration of submicron fraction (0.3-1 µm) from 31st of March until 6th of April 2015. Moreover, knowledge on occupational exposure to coarse particles originating mainly from welding activities is currently very limited (Iavicoli, et al., 2013; Lin et al., 2015). Thus, another aim of this study is to assess workers’/students’ exposure to large particles (PM₁₀) inside a workshop area of an educational building (Department of Physics, the University of Jordan). In addition, a simple indoor aerosol model was used in order to estimate the loss rate and the emission rate of aerosol particles inside the workshop area.

METHODS

The number size distribution of particles between 300 nm and 10 µm was measured by using an Optical Particle Sizer (TSI OPS 3330, 13 size-bins, 1 minute time resolution, 1 L min⁻¹ flow rate, and dead-time correction). The instrument was calibrated by the manufacturer and it was located in the metal and welding section of the workshop area, 2.5 m from the windows. The indoor and outdoor air sampling was performed directly without additional tubing at a height of about 1.6 m above the ground, which represented the breathing zone.

The dynamic behavior of indoor aerosols can be described by the mass-balance equation (Nazaroff, 2004; Hussein and Kulmala, 2008). In its simple form, it requires aerosol particle concentrations outdoors, indoor domain geometries, ventilation rate, penetration efficiency, dry deposition, and additionally a source term that represents particle formation and emission indoors. Mathematically, this is written as:

\[
\frac{dI}{dt} = \lambda PO - (\lambda + \lambda_d)I + ER
\]

(1)

where I and O are the aerosol particle concentrations indoors and outdoors, respectively, P is the penetration factor of aerosol particles across the building shell (natural ventilation) or a standard filter installed in a mechanical ventilation system, λ is the ventilation rate, λ_d is the deposition rate of aerosol particle onto available indoor surfaces, and ER is the emission rate of aerosol particles indoors. This mass-
balance equation describes a certain particle size-fraction where aerosol particles have rather similar physical properties.

Although this mass-balance equation is primarily used to simulate and predict the indoor aerosol particles and their behavior, it can be used in inverse modeling to estimate some parameters such as P, λ, λd or even ER (Mølgaard et al., 2014; Hussein et al., 2015b). It was utilized in the current study to understand the loss rate of aerosol particles, according to the principles described by Hussein (2014) and Hussein et al. (2015a). Subsequently, the emission rates were estimated, which in this case was the production rate of aerosol particles, according to the semi-empirical approach described by Hussein et al. (2015b).

As a simple health risk assessment for the exposure of the workers/students to large particles (1-10 µm), the deposited dose was considered which is defined as the amount of aerosol particles deposited in the respiratory system while breathing. The deposited dose was calculated based on particle mass according to Hussein et al. (2013; 2015b):

$$D_{deposited} = \int_{t_1}^{t_2} \int_{D_{p1}}^{D_{p2}} V_E \cdot DF \cdot n_N^0 \cdot f \cdot d\log D_p \cdot dt$$

(2)

where VE ([L min⁻¹] or [m³ h⁻¹]) is the minute ventilation (known also as volume of air breathed per time), DF [---] is the respiratory deposition fraction of aerosol particles and $n_N^0 = \frac{dN}{d\log(D_p)}$ [particles cm⁻³], where $D_p$ is the particle diameter, is the lognormal particle number distribution. It should be noted that both DF and $n_N^0$ are functions of log($D_p$). $f$ is a dose metric such as the particle surface area ($\pi D_p^2$) or particle mass ($\rho_p D_p^3$). In our case $f$ is the particle mass. The integrals are evaluated during an exposure time period $\Delta t = t_2 - t_1$ to large particles (1-10 µm) on any time resolution.

The volume air breathed per time (i.e. the minute ventilation), VE, is strongly associated with the body size (Bennett and Zeman, 2004), the activity, the age and the breathing frequency of the substance (Holmes, 1994; ICRP, 1994). Values for the volume air breathed per time used in this study were adopted from Holmes (1994) and Hussein et al. (2013).

The respiratory deposition fraction, DF, is defined as the probability of aerosol particles to deposit in the respiratory system and it strongly depends on the gender and the activity level of the subject (Löndahl et al., 2007). Moreover, the same group reported that the size range and the hygroscopicity of aerosol particles affect the DF. In particular, they pointed out the smaller the particle is the higher the DF is expected to be. Due to the fact that the relative humidity in the respiratory system and, more specifically, in the lungs is approximately 99.5% (Ferron et al., 1988; Anselm et al., 1990), the diffusion rate and the DF of hygroscopic particles decrease (Löndahl et al., 2007). Moreover, since the respiratory system consists of the head/throat, tracheobronchial and the pulmonary/alveolar region, the respiratory deposition fraction varies accordingly (ICRP, 1994; Löndahl et al., 2007). For our calculations, the respiratory deposition fraction values were taken from the GMD (deposition) curve of large particles (1-10 µm) as presented by Hussein et al. (2015b).

**CONCLUSIONS**

During the weekend, $PN_{0.3-10}$ varied from 12.86 to 64.64 cm⁻³ and during the weekdays from 23.13 to 4162.44 cm⁻³ (Fig. 1). $PM_{0.3-10}$ ranged between 1.68 and 13.58 µg m⁻³ and from 1.15 to 596.60 µg m⁻³ during the weekend and the weekdays, respectively (Fig. 2).

With respect to concentrations during weekdays, our findings indicated that the highest mean and median $PN_{1-10}$ ($PM_{1-10}$) and $PN_{0.3-1.0}$ ($PM_{0.3-1.0}$) concentrations were observed during the operation of the welding machine, followed by the activity of iron welding without the simultaneous use of the exhaust fan and also
with the running of the exhaust fan afterwards. The maxima PN$_{10}$(PM$_{10}$) and PN$_{0.3}$ (PM$_{0.3}$) concentrations were detected when iron welding took place, and later the operation of the exhaust fan and the activity of iron sorting/drilling occurred.

When the workshop area was open and occupied, the (average) particle number loss rate for submicron particles (0.3−1 µm) fluctuated from 0.24±0.01 to 2.01±0.07 h$^{-1}$ and for micron particles (1−10 µm) from 0.35±0.01 to 2.11±0.05 h$^{-1}$. Furthermore, the (average) particle number emission rate for micron and submicron particles ranged from 75-1008 particles×h$^{-1}$×cm$^{-3}$ and 5.74×10$^4$-9.31×10$^4$ particles×h$^{-1}$×cm$^{-3}$, respectively.

It is believed that variations in the PM and PN concentration between submicron (0.3−1 µm) and micron (1−10 µm) particles during the different activities could be attributed to the ventilation rate of the room and the time spent in the room in addition to the effect of occupancy of the workshop area. The type of the activities themselves could have also played a significant role. However, further study is required in order to confirm these speculations and to determine fully the physicochemical characteristics of particles measured in similar environments.

Moreover, as simple exposure assessment to large particles (PM$_{10}$) the deposited dose in the respiratory system based on particles mass was calculated for a male adult. In particular, the findings of this research showed that during two events for which it was assumed that the workers were only standing, the head/throat region received the largest fraction of the total deposited dose followed by the alveolar and the tracheobronchial region. (Table 1). On the other hand, during two events for which it was considered that the workers performed light exercise, the alveolar and the head/throat region received the majority and the smallest fraction of the total deposited dose, respectively (Table 1).

We should bear in mind that the reported values of the deposited dose in this study represent an estimation of the minimum amount of the deposited dose in the respiratory system of a male adult during standing/resting and performing light exercise. To improve exposure assessments as well as to fill the gaps in health effects of aerosol particles, the use of indoor aerosol models (IAM’s) in combination with modeling the deposited dose is highly recommended.

Figure 1: Particle number concentrations (Time series based on a 1-minute resolution).
Table 1. Deposited dose [µg] of large particles (PM$_{10}$) based on particle mass calculated for an adult male during four events (Event 1, 4, 6 and 9).

<table>
<thead>
<tr>
<th>Respiratory regions</th>
<th>Event 1 (Making coffee, smoking and having lecture)</th>
<th>Event 6 (Making coffee)</th>
<th>Event 4 (Fan &amp; machine on, welding iron without fan)</th>
<th>Event 9 (Metal turning)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activities</td>
<td>Activities</td>
<td>Activities</td>
<td>Activities</td>
</tr>
<tr>
<td>Head</td>
<td>24.45</td>
<td>5.18</td>
<td>24.06</td>
<td>5.26</td>
</tr>
<tr>
<td>Tracheobronchial</td>
<td>2.40</td>
<td>0.51</td>
<td>38.09</td>
<td>8.33</td>
</tr>
<tr>
<td>Alveolar</td>
<td>11.53</td>
<td>2.44</td>
<td>70.16</td>
<td>15.34</td>
</tr>
<tr>
<td>Total</td>
<td>38.38</td>
<td>8.13</td>
<td>132.31</td>
<td>28.93</td>
</tr>
</tbody>
</table>

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INTRODUCTION

The responses of carbon cycle of boreal ecosystems to changing climate is an open question of both global as well as regional importance that can be studied with land surface schemes (LSSs) that explicitly resolve terrestrial carbon cycle processes. JSBACH (Reick et al., 2013), the LSS of the earth system model (ESM) of German Max Planck Institute (MPI-ESM, Roeckner et al., 2006), includes sophisticated descriptions of vegetation photosynthesis and soil processes. Here we apply JSBACH for a domain covering Finland to assess the carbon cycle processes through the past decades and by the end of the ongoing century. In this work we inspect the impact of climate and atmospheric CO$_2$ concentration trends on photosynthetic gross primary production (GPP) and the length of vegetation active period (VAP) during this century.

METHODS

JSBACH model can be driven either as a global land surface module of MPI-ESM or by forcing it offline with prescribed climate data. Here we applied the model regionally for Finland and adopted the daily climate variables for years 1980 to 2099 from nine CMIP5 model simulations that were bias corrected with FMI gridded homogenized data (Aalto et al., 2016). Five of the selected CMIP5 model runs followed RCP4.5 emission scenarios and four of them RCP8.5 emissions. A quantile-quantile type bias correction was used for relative air humidity, shortwave radiation, wind speed and daily minimum and maximum temperatures (Räisänen and Räty, 2013) and a parametric quantile mapping method (Räty et al., 2014) for daily precipitation. Because of the lack of reference data, incoming longwave radiation was just downscaled to the impact model grid without any correction for possible biases. Global mean CO$_2$ concentrations from the RCPs 4.5 and 8.5 were linearly interpolated to monotonously increase through the calendar years.

Model internal timestep was set to 1 hour. The spatial resolution of the model run was that of the surface boundary data (0.1°x0.1°). Number of the soil layers was set to five and that of the plant functional types (PFTs) to 22 out of which less than half exists in Finland. Because according to Böttcher et al (2016) the start date of the photosynthetically active season (SOS) of coniferous evergreens in the model is ahead of the observed, an air temperature sum based downregulation of photosynthetic capacity was implemented to JSBACH. Moreover, Böttcher et al. (2016) showed that the modeled SOS of deciduous broadleaf species in Finland is generally behind the observed and thus the threshold temperature of the temperature sum regulating the bud-break was decreased from 4°C to 2°C in the model.
The running sequence consisted of four different spin-up phases that were run prior to the transient production run throughout the forcing data timeseries. In the first phase the CO2 concentration was set to that of the year 1852 (285 ppm) and the model was run for 30 years with the climate from 1980 to 2010. This round was made to make sure that the relatively slowly changing state variables in the system reached a semi-equilibrium with the current day climate. The second phase was started from the equilibrium reached during the first round. The atmospheric CO2 concentration and the climate were equal to those of the first round and the purpose of this round was to produce thirty years of driving data for the following phase. The third phase of the spin-up was performed to develop soil carbon storages using the net primary productivity (NPP) estimated at the second phase. In this phase soil carbon model YASSO was run offline from the other biogeochemical and biophysical processes in JSBACH model framework.

The fourth running phase used the carbon, water and energy states equilibrated with CO2 concentration of mid 19th century and current day climate during the previous steps. In this phase the climate from 1981 to 2010 was circulated for 120 years with the increasing atmospheric CO2 concentrations from 1851 to 1979. Finally the production run from 1980 to 2099 is started from the state reached at the fourth spin-up phase. The first year 1980 is excluded from the analysis in order to have a continuous driving data series preceding the first included year 1981.

To assess the impact of climate change on the length of the vegetation active period (VAP) we applied the method introduced in Böttcher et al. (2014, 2016) to estimate the yearly start and end of the photosynthetically active period (SOS and EOS) from the GPP timeseries. The resulting timeseries of SOS, EOS and GPP were areally averaged for 11 Finnish forest vegetation zones.

CONCLUSIONS

Figure 1. Daily GPP timeseries (green) through years 1981 to 2099 averaged over the Finnish forest vegetation zones 2b (left) and 4b (right). Yearly SOS and EOS are indicated with red and blue dots, respectively. Forcing meteorological data is adopted from a RCP4.5 run performed with CanESM2.
Figure 2. The same as in the Figure 1. but the forcing meteorological data is adopted from a CNRM-CM5 RCP4.5 run.

The GPP timeseries and the respective SOS and EOS dates estimated from run forced with data from two ESMs under RCP4.5 show that the length of VAP in the south is longer than in the north and it will increase throughout Finland (Figures 1 and 2) during the ongoing century. In both areas and models shown, the lengthening of VAP takes place both in the beginning and in the end of the season. However, the rates of the changes vary according to the area and the forcing model. The higher year to year variability of SOS than that of EOS owes to high sensitivity of SOS to the air temperature whereas EOS is limited by the availability of sun light and thus it is less variable and shows weaker trend towards the end of the century.

The decreasing trend of SOS (not shown) through the timeseries (1981-2099) is significant with $p<0.0001$ in all of the model runs throughout Finland. The increasing trend of EOS is significant with $p<0.0001$ everywhere in Finland in all but one model run (forced with a RCP4.5 ESM simulation) where there are small areas of less significant trend. In addition to VAP specific indices, other vegetation related climate change indices, including heterotrophic and autotrophic respiration, net ecosystem carbon exchange, soil moisture index, water use efficiency and surface albedo, have been retrieved from the model data.

ACKNOWLEDGEMENTS

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HIGH SOIL PHOSPHORUS CONCENTRATION DEFINES GROUND VEGETATION COVER COMPOSITION IN SUBARCTIC FORESTS

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Keywords: VEGETATION, PHOSPHORUS, SOIL, CLIMATE

INTRODUCTION

Although nitrogen (N) usually limits growth in boreal forests (e.g. Helmisaari 1995, Nilsen 2001, Korhonen et al. 2013, Coucheney at al. 2013), these forests can also suffer from deficieny or co-limitation of phosphorus (P) (Shaver et al. 1998, Moilanen et al. 2010, Vadeboncoeur 2010, Crowley et al. 2012). Phosphorus is one of the most immobile major nutrients (Hinsinger 2001), and one of the most recycled nutrients in boreal forests. At least for Scots pine (Pinus sylvestris) this recycling is stronger at higher latitudes of origin (Oleksyn et al. 2003). Climate change will most likely alter the nutrient cycling of forests. What this effect will be is still somewhat unclear, as some studies suggest that soil warming causes accelerated microbial activity and release of nutrients (Rustad et al. 2001, Robinson et al. 2002), while others have found it to reduce soil moisture, which slows down decomposition (Hicks Pries et al. 2013).

Our study area is located in Eastern Lapland, near Sokli, where a large carbonatite massif lies. The forests in Sokli differ greatly from the typical forests of the region by being dominated by Downy birch (Betula pubescens) and having many grasses growing in the understory. Generally the forests of the region are Scots pine or Norway spruce (Picea abies) dominated or a mixture of the three tree species with understory dominated by dwarf shrubs. In addition to the massif in Sokli there are so-called hot spots of P in various other places. Part of our plots have been set up to places which, by visual estimation of vegetation, were evaluated as possibly high in soil P. The rest of the plots are in forests with a vegetation cover typical for the region. This arrangement allowed us to compare different levels of soil P without organizing any fertilizer experiments. We wanted to first examine whether we truly had found plots with high soil P based on the visual estimation, and how the high soil P is related to the vegetation cover. We also wanted to see if we could find a relationship between soil nutrient content and needle nutrient content, as needles are commonly used in studying nutrient conditions of forests. We hypothesized that 1) high soil total P causes high needle and leaf P concentrations, and 2) the percentage cover of certain plant species in ground vegetation is higher in soils rich in P compared to soils with lower P.

METHODS

We set up altogether 16 research plots in and around Värrö Strict Nature Reserve, which is located about 6 km from Sokli. Each plot consisted of sub-plots for ground vegetation cover survey and soil sampling. We also took needle and leaf samples and measured the trees at each plot. We analyzed total elemental concentrations of all soil, needle and leaf samples with ICP-OES. Total C and N were analyzed from all organic samples with VarioMax. In addition, rainwater and snow samples were taken monthly during October 2014-September 2015 for determining if there is any aerial deposition of P. The soil, needle and leaf samples were taken in summer and fall 2015. Ground vegetation cover was inventoried during 2014 and 2015 and tree composition in 2015. Rainwater and snow samples were analyzed with ion chromatography at Finnish Meteorological Institute. Based on the ordination of the ground vegetation data
(by the global non-metric multidimensional scaling (NMDS)) we found a connection between ground vegetation cover and soil P concentrations. Consequently we built a statistical model explaining this relationship.

CONCLUSIONS

The total P concentrations in the soil of most of our plots were within the range given in the literature (Vance et al. 2003, Jones and Oburger 2011), but the plots we expected to have high soil P truly had high soil P concentrations. However, the highest soil P could in most cases be found in the uppermost soil layer. This indicates that the source of P is not the bedrock, but perhaps decaying plant material. This is supported by the result that downy birch leafs and litter have higher P concentration than conifer needles, and downy birch was the dominating tree species at high P plots. Aerial deposition of P was basically non-existent, excluding it as a source of P. With high soil P the amount of forbs (e.g. Rubus arcticus) and grasses increased in ground vegetation. Needle P concentrations didn’t differ significantly between plots. Norway spruce needles showed higher concentrations of total P than Pinus sylvestris needles, which was expected based on literature (Mellert and Göttlein 2012, Oleksyn et al. 2003).

Mean air temperature measured at Värrö Research Station has risen notably within the last decades. Rising mean annual temperature can alter soil microbial activity and allow for changes in the release of nutrients. This can lead to drastic changes in vegetation composition by changing the dynamics of current species. Experimental warming in the low Arctic (Walker et al. 2006) resulted in increased amounts and heights of forbs and graminoids (grasses). On the other hand the same study found that warming increased the dominance of woody plants as well as the height of shrubs. They might, thus, overshadow at least some of the forbs and graminoids. Other warming studies in Alaska revealed increased woody shrub production (Chapin et al. 1995, Chapin and Shaver 1996), and a remote sensing study using over 30 years of data (Park et al. 2016) found circumpolar greening of the Arctic as the growing season has extended and biological production increased. In nutrient rich spots these changes could be even more pronounced. Better understanding of ecosystem functions in the vulnerable subarctic region are needed, as changes in vegetation can modify atmosphere-biosphere feedbacks as well as possibly allow for invasive species to enter more easily.

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ANTHROPOGENIC BLACK CARBON EMISSIONS IN ICELAND: CONCENTRATIONS OBSERVED IN SNOW AND GLACIER ICE IN SOUTHERN ICELAND

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Keywords: BLACK CARBON, ORGANIC CARBON, DUST, ARCTIC, DEPOSITION, SNOW MELT

INTRODUCTION

Black carbon (BC, soot) particles are short-lived climate forcers (SLCF). With relatively short life time in the atmosphere (from days to weeks), BC impacts vary regionally. In the European Arctic, the land areas belong to the five Nordic countries of Denmark (including Greenland and the Faroe Islands), Finland, Norway, Sweden and Iceland. Earlier, BC in air and snow in the background areas has been investigated and assessed largely in the other Nordic countries (AMAP 2015), except in Iceland.

Over 80 % of the total energy consumption in Iceland is produced with domestic renewable water and geothermal power and therefore Icelandic snow and ice are not expected to contain high concentrations of BC in background areas.

Figure 1. The Solheimajökull glacier surface snow and ice were sampled in 2016 and 2017. Our research question is whether soot is a significant contributor to snow and glacier melt in Iceland.

Glaciers in Iceland are melting rapidly. In the Arctic region, the albedo feedback mechanism, e.g., due to deposited BC, can accelerate snow and ice melt (Bond et al. 2013). We have sampled snow and glacier ice
in southern Iceland in March 2016 (Meinander et al. 2017) and March 2017 (new results, no citations available) (Fig. 1), for the analysis of their BC concentrations. The official CLRTAP national BC emission inventory of Iceland (available at http://cdr.eionet.europa.eu) is used to understand and explain the results.

METHODS

Our field work included sampling in multiple locations in southern Iceland in March 2016 and March 2017, including the glacier Solheimajökull. The mass balance of this glacier is negative and it has been shrinking during the last 20 years by 900 meters from its southwestern corner. The BC on snow filters were analyzed at the Finnish Meteorological Institute (FMI) with a Thermal/Optical Carbon Aerosol Analyzer (OC/EC) (Figure 2). More detailed description of the methods used can be found, e.g., in Meinander et al. 2013. The BC emissions data for Iceland were gained from http://cdr.eionet.europa.eu.

Figure 2. The snow and ice samples were melted and filtered (left), and the filters were then analysed at the Finnish Meteorological Institute using Thermal/Optical Carbon Aerosol Analyzer (OC/EC, right).

CONCLUSIONS

The samples collected bi-annually from the glacier surface snow and ice contained < 12 ppb of BC, while higher BC amounts, up to 203 ppb, were found in snow samples closer to roads (Table 1). The glaciers in Iceland are rapidly melting, but our results show no significant concentrations of BC in glacier snow or ice samples originating from the southern Iceland.

Table 1. Summary of black carbon (elemental carbon, EC) concentrations [ppb] observed in snow and glacier ice in 2016 and 2017 in Iceland, based on our preliminary results.

<table>
<thead>
<tr>
<th>Year</th>
<th>EC in glacier [ppb]</th>
<th>EC closer roads [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2016</td>
<td>&lt; 12</td>
<td>&lt; 203 (old snow)</td>
</tr>
<tr>
<td>2017</td>
<td>&lt; 4</td>
<td>&lt; 70 (new snow)</td>
</tr>
</tbody>
</table>

Energy production utilizing combustion processes, especially small scale residential heating, is an important source of BC in other Nordic countries. However, in Iceland over 80% of the total energy consumption is produced with domestic renewable water and geothermal power, and therefore the BC emissions from this source are minimal (Table 2). Other potential BC sources in Iceland include agricultural burning, industry (aluminium and ferroalloy production and fishing industry), open burning, residential heating and transport (shipping, road traffic, aviation). We compared the emissions per capita to be less than half of any other Nordic country, and the total BC emissions in Iceland to be less than 1/10 of any other Nordic country (the data for the other Nordic countries not presented here).
Table 2. Anthropogenic BC emissions in Iceland based on fuel sold. Calculated on the basis of European Environmental Agency (http://cdr.eionet.europa.eu) for the emissions, and World Bank for the population data.

<table>
<thead>
<tr>
<th>Year</th>
<th>National total BC emissions [kt/y]</th>
<th>BC emission per capita [kg/y/capita]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>0,1268</td>
<td>0,43</td>
</tr>
<tr>
<td>2010</td>
<td>0,1239</td>
<td>0,39</td>
</tr>
<tr>
<td>2015</td>
<td>0,1935</td>
<td>0,58</td>
</tr>
</tbody>
</table>

Figure 3. The contribution of the various sources for the Iceland’s BC emissions in 2015, based on the official CLRTAP national emission inventory of Iceland. Ten biggest sources from bigger to smaller (the original sources given in the inventory here summed up, as explained): I_Offroad: Mobile Combustion in manufacturing industries and construction, F_RoadTransport = All transport; I_offroad = National fishing; B_Industry = Aluminium production; J_Waste = All waste; G_Shipping = National navigation (shipping); B_industry = Iron, steel and ferroalloys production and other mineral products; H_aviation = International aviation LTO (civil); A_PublicPower = Public electricity and heat production; E_Solvents = Other product use. In addition, Road paving with asphalt and Domestic aviation LTO (civil) are included in the diagram with values < 0.1 E-5 kt/y. Figure drawn based on the data available at http://cdr.eionet.europa.eu.

Highest concentrations of BC on snow and ice were found close to roads. Snow and ice on the glacier Solheimajökull contained minimum amounts of BC, but visible amounts of black dust and large amounts (thousands of ppb) of organic carbon. Hence, the radiative forcing effects due to BC in Iceland are expected significantly smaller compared to other countries or the Arctic (see e.g., Hienola et al. 2016).

Icelandic soils are formed from the volcanic deposits (Arnalds 2015). Icelandic andosols store more organic carbon reserves per unit area than other dryland soils. Upper layers of these soils can be transported with winds, often during the winter, and deposited on snow and glaciers as previously observed (Dagsson-Waldhauserova et al. 2015).

Soot particles deposited in the cryosphere can absorb solar irradiance and accelerate melting of snowpacks and glaciers via the snow albedo feedback mechanism (Bond et al. 2013). Additionally, deposited light-absorbing aerosols, such as soot, can decrease the water-holding capacity of melting dirty snow, resulting in...
in decrease in snow density, causing ‘the density effect’ (Meinander 2014, Skiles & Painter 2016, Table 3).

On the contrary, our previous experimental results on Icelandic volcanic ash (Dragosics et al. 2016, Table 3) have showed that Eyjafjallajökull ash with grain size smaller than 500 µm insulate the ice below at a thickness of 9-15 mm (called as ‘critical thickness’). For the 90 µm grain size, the insulation thickness was found to be13 mm. The maximum melt occurred at thickness of 1mm for the larger particles, and at the thickness of < 1-2 mm for the smaller particles (called as ‘effective thickness’). Earlier, similar threshold dust layer thickness values have been given for Mt St Helens (1980) ash, and Hekla (1947) tephra, but our results were the first ones reported for the Eyjafjallajökull ash. In Iceland, the dust layers in the nature can be from mm scale up to tens of meters. Our results were recently repeated and confirmed by Möller et al. (2016).

<table>
<thead>
<tr>
<th>Cryospheric effect</th>
<th>Impurity</th>
<th>First suggested in</th>
<th>Cited and supported in</th>
</tr>
</thead>
</table>

Table 3. The cryospheric effects of aerosols deposited on snow and ice, first reported in the experiments at the Finnish Meteorological Institute (Dragosics et al. 2016 work supervised by Meinander O at FMI), and the research citing and confirming these findings.

This study showed the first results on BC observations from snow and glacial ice in Iceland, a remote background area of the European Arctic. The BC concentrations were generally low, but increased closer to anthropogenic sources, such as roads. Icelandic snow and glacial ice contained, however, large amounts of organic carbon and volcanic dust. Icelandic soils, andosols, are different to other Scandinavian soils, and contain high amounts of organic carbon. Iceland is also the largest desert in both Europe and the Arctic where volcanic desert dust is frequently suspended and deposited on snow and glaciers. Frequent explosive volcanic eruptions provide high amounts of volcanic ash deposited on glaciers due to the location of the volcanoes in the vicinity of the glaciers or beneath them.

Our results indicate that rapid glacial melting in Iceland would not be accelerated due to BC deposition. Instead of BC, we suggest that one of the main glacier melting triggers (in addition to Arctic warming), can be organic material and volcanic dust and ash (i.e., so-called high latitude dust HLD, see Bullard et al. 2016) on the glacier surface. On the basis of our observations, in Iceland the radiative forcing effects due to dust and organic carbon can be bigger than that of BC, and need to be assessed more in detail.

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DOES INCREASING TEMPERATURE INCREASE CARBONACEOUS AEROSOL DIRECT RADIATIVE EFFECT OVER FORESTS?

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Keywords: remote sensing, climate modelling, aerosol, land surface temperature.

INTRODUCTION

Aerosols are an important regulator of the Earth’s climate. They scatter and absorb incoming solar radiation and thus cool the climate by reducing the amount of energy reaching the atmospheric layers and the surface below (direct effect) (e.g. Charlson et al., 1992). A certain subset of the particles can also act as initial formation sites for cloud droplets and thereby modify the microphysics, dynamics, radiative properties and lifetime of clouds (indirect effects) (Albrecht, 1989; Twomey, 1991; Stevens and Feingold, 2009). The magnitude of aerosol radiative effects remains the single largest uncertainty in current estimates of anthropogenic radiative forcing (IPCC, 2013).

One of the key quantities needed for accurate estimates of anthropogenic radiative forcing is an accurate estimate of the radiative effects from natural unperturbed aerosol. The dominant source of natural aerosols over Earth’s vast forested regions are biogenic volatile organic compounds (BVOC) which, following oxidation in the atmosphere, can condense onto aerosol particles to form secondary organic aerosol (SOA) and significantly modify the particles’ properties. In accordance with the expected positive temperature dependence of BVOC emissions (Penuelas and Staudt, 2010; Duncan et al., 2009), several previous studies have shown that some aerosol properties, such as mass concentration and ability to act as cloud condensation nuclei (CCN), also correlate positively with temperature at many forested sites (e.g. Tunved et al., 2006; Leaitch et al., 2011; Paasonen et al., 2013). The evidence for an effect of temperature on aerosol direct effects due to increased BVOC emissions, however, is less clear.

The main objective of this study was to investigate the effect of increasing temperatures on the aerosol direct radiative effect, and to provide a quantitative estimate of this effect and of the plausible negative feedback in a warming climate. More specifically, we investigated the causes of the positive correlation between aerosol optical depth (AOD) and land surface temperature (LST) over the southeastern US and boreal forests where biogenic emissions are a significant source of atmospheric particles.
METHODS

The study was done using a combination of satellite data and climate modelling. Key remote sensing data used were the aerosol optical depth and land surface temperature products available from the ESA Aerosol-CCI and GlobTemperature projects, together with ancillary data, such as column concentrations of carbon monoxide (CO), nitrogen dioxide (NO$_2$) and land cover type. For the modelling work we utilized the aerosol-chemistry climate model ECHAM-HAMMOZ, which describes all known relevant atmospheric aerosol processes.

The core data sets for this study were provided by the Advanced Along Track Scanning Radiometer (AATSR) that flew on the ESA polar orbiting Environmental Satellite ENVISAT (2002-2012). We used daily Level 3 AOD retrievals done with the ADV algorithm (Kolmonen et al., 2016). The Level 3 LST data (Prata, 2002) with higher resolution ($0.01 \times 0.01$ degrees) was regridded to $1 \times 1$-degree resolution to match the resolution of the AOD data.

AOD retrieved from satellite radiance data contains contributions from all aerosol types present in the atmospheric column. To discriminate natural contributions to the AOD from other contributions (such as aerosol particles emitted by forest fires or pollution transported from elsewhere), we used ancillary data. We used daily Level 3 CO column concentration data retrieved from NASA's Atmospheric Infrared Sounder (AIRS) instrument for the years 2002-2012. CO is the best proxy for biomass burning aerosols available from satellite-based measurements. In addition, we utilized tropospheric NO$_2$ observations from the Ozone Monitoring Instrument (OMI). NO$_2$ was used to identify aerosols that are mixed with anthropogenic pollution. Daily Level 3 OMI NO$_2$ data were available from 2005 onwards.

In order to estimate the effect of SOA on the AOD-LST relationship, we applied the ECHAM6-HAMMOZ aerosol-chemistry climate model (Stier et al., 2005; Zhang et al., 2012; Bergman, et al. 2012; Laakso et al. 2016). Biogenic VOC emissions are computed online using the Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al., 2006). MEGAN determines emissions of terpenes and isoprenes as a function of temperature, available solar radiation, soil moisture, and carbon dioxide concentration (for which a fixed global average is used). In order to couple MEGAN emissions with atmospheric SOA formation in the model, a scheme based on the volatility basis set (VBS) (Donahue et al., 2011) was introduced. It enabled the modelling of the condensation and evaporation of semi-volatile organic compounds (sVOC). These schemes enabled the simulation of the effects of temperature changes on atmospheric aerosol load. For biomass burning, the Global Fire Emissions Database (GFEDv2) was used. Model’s large scale circulation in our simulations was nudged towards ECMWF reanalysis data (ERA-Interim; Berrisford et al., 2011) to ensure compatibility between the model and the observed atmospheric conditions. The simulation period was 2002-2010 with a three month spin-up.

To estimate how different aerosol sources affect the aerosol load over the studied regions, four simulations were performed:

1) CONTROL (all the schemes described above are in use);
2) noBIOSOA (same as CONTROL but without biogenic SOA formation);
3) noBB (same as CONTROL but without biomass burning emissions);
4) noAQSOA (same as CONTROL but without SOA formed in aqueous phase).

To study the aerosol feedback effect in the future, two simulations from 2045 to 2055 using the RCP8.5 scenario for the year 2050 were made: 1) FUTURE_CONTROL: all the schemes described above are in use, monthly averages, 2) FUTURE_noBIOSOA: same as CONTROL but without biogenic SOA formation, monthly averages. The RCP8.5 scenario was chosen because it represents the highest temperature increase in the scenarios and thus it provides the best opportunity to detect and quantify a globally significant negative aerosol feedback.
CONCLUSIONS

In this study we estimated the AOD-LST dependency over the several forested regions and approximated the radiative effects of this dependence. The studied regions were in: southeastern US (70-90°W, 30-37.5°N), Canada (80-130°W, 50-63°N) and Russia (40-65°E, 59-66°N and 78-100°E, 57-63°N). Over these regions, the observations and simulations produced corresponding results. Table 1 presents the direct radiative effect estimates for the biogenic aerosols based on the observations and simulations. The observational and simulated radiative effect estimates are in good agreement and show that the radiative effects are the largest in the vicinity of anthropogenic sources in mixed forests in Western Russia and southeastern US. The main conclusions of this study are:

- AOD exhibits temperature dependent behaviour which is most likely caused by biogenic emissions in all the studied regions.
- The temperature dependence of biogenic AOD is stronger in the presence of anthropogenic aerosols.
- The temperature dependent biogenic AOD has significant radiative effects in the present day climate but the significance might decrease in the future, thus biogenic aerosols may not produce a strong negative climate feedback. This contradicts with the hypothesis that increased biogenic emissions in the future could slow down global warming.

Table 1. Direct radiative effects of biogenic aerosols in four forested regions. The acronyms ENF and MF refer to evergreen needleleaf forest and mixed forest, respectively. Subscripts obs and sim refer to observations and simulations, respectively.

<table>
<thead>
<tr>
<th>Region</th>
<th>DRE$_{\text{obs}}$ [W/m$^2$/K]</th>
<th>DRE$_{\text{sim}}$ [W/m$^2$/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE US</td>
<td>-0.31±0.22</td>
<td>-0.34±0.02</td>
</tr>
<tr>
<td>Canada</td>
<td>-0.21±0.36</td>
<td>-0.138±0.002</td>
</tr>
<tr>
<td>Eastern Russia</td>
<td>-0.15±0.07</td>
<td>-0.17±0.01</td>
</tr>
<tr>
<td>Western Russia, ENF</td>
<td>-0.29±0.03</td>
<td>-0.25±0.01</td>
</tr>
<tr>
<td>Western Russia, MF</td>
<td>-0.41±0.07</td>
<td></td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENTS

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MULTIVARIATE STATISTICAL MODELS IN THE ANALYSIS OF NEW PARTICLE FORMATION AND GROWTH MEASUREMENT DATA IN PO VALLEY, ITALY – QUANTIFYING THE ROLE OF ORGANICS, AMMONIA AND SULPHURIC ACID

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Keywords: New particle formation, organics, sulphuric acid, ammonia, mixed layer height.

INTRODUCTION

Characterization the new particle formation (NPF) events and the chemistry of particles during the growth phase was the main purpose of an intensive atmospheric measurement campaign conducted at the polluted rural site, San Pietro Capofiume (SPC) station in the Po Valley, Italy. The measurements were part of the joint Supersito and PEGASOS project, taking place from June 9th to July 10th 2012. Measurements included aerosol size distributions down to 1.6 nm, properties and composition of particles, concentrations of gases and several meteorological parameters. Sulphuric acid concentration was not measured during the studied period and, therefore, it was calculated with proxy function introduced in Mikkonen et al. (2011a). The proxy was based on measured SO2 concentration, solar radiation, condensation sink and relative humidity.

Various factors have been shown to affect NPF and subsequent growth in atmospheric conditions in SPC. This study will continue the work of two such papers; Kontkanen et al. (2016), who studied mainly formation and growth of sub 3nm clusters and Mikkonen et al. (2011b) who studied the effect of various meteorological and trace gas variables on the NPF and the growth of newly formed particles to potential CCN sizes. With the extensive set of measurement instruments available in the PEGASOS campaign we will be able to get better characterisation of the physical and chemical properties of new particle formation events.

METHODS

In the data-analytical point of view, studying the effects of meteorological and trace gas measurement data on the new particle formation and growth is a subject of causal inference. The effects cannot be computed from the data alone, nor from the distributions that govern the data. The causal assumptions, the study design and the data are the elements required for scientific inference in empirical research. Atmospheric measurement data holds great number processes that are well defined by their physical and chemical properties. However, remarkable number of reactions, and especially their relevance on the NPF and subsequent growth of the formed particles, are not known. These processes can be detected with explorative-type data analysis conducted on extensive datasets. We applied Structural Equation Model (SEM, Hoyle 2012) on our measurement data, in order to find the effects and reaction paths leading from measured gas phase variables to formation and growth of new aerosol particles. Measured ammonia
concentration, sulphuric acid proxy, mixed layer height and other meteorological factors were first set to the SEM model with the new particle formation rate ($J_{1.6}$) and growth rate (GR). Concentrations of organic compounds were not measured and thus their effect on particle formation and growth was initially estimated from the residuals of a regression model predicting the growth rate with $H_2SO_4$-concentration. Particle formation rate $J_{1.6}$ was calculated in Kontkanen et al. (2016) and growth rate (GR) was calculated with two different methods. Firstly, from the positive ion size distribution introduced in Kontkanen et al. (2016) for size ranges of 1.6-3nm, 3-7nm and 7-20nm, and secondly, based on SMPS data by following the evolution of peak mean diameter of the growing nucleation mode particles (Hamed et al. 2007). Daily averages of the predictor variables for the statistical models were calculated within period of 8am-4pm for analysing the factors affecting to day-by-day variations of $J_{1.6}$ and GR. This period was chosen since NPF is observed in SPC during these hours (e.g. Hamed et al. 2007).

A monodisperse particle growth model MABNAG (Model for acid-base chemistry in nanoparticle growth; Yli-Juuti et al., 2013) was used to calculate the contribution of ammonia and sulphuric acid to the particle growth and to estimate how large particle mass fraction and gas phase concentrations of organics would be needed to establish the growth seen in the measurements. MABNAG includes representation of condensation and the particle phase acid-base chemistry.

RESULTS AND CONCLUSIONS

The results of a multivariate regression model indicated that sulphuric acid and ammonia could explain roughly half of the variation of $J_{1.6}$ between NPF days. The results from the MABNAG growth model, shown in Figure 1, indicate that organics were the main component in modelled mass fractions. Both of these results highlights the importance of organics in the NPF process. These results are in line with several recent studies, e.g. Tröstl et al. (2016) who have suggested that low-volatility organic vapours contribute significantly to initial growth of newly formed particles.

![Figure 1. Mass fraction as a function of particle diameter predicted with the MABNAG model showing that organics are the main factor driving particle growth.](image)

In addition to daily formation rates, Kontkanen et al (2016) presented diurnal variation of $J_{1.6}$. For the rapidly fluctuating formation rate the predicting ability of regression model containing ammonia and sulphuric acid was even lower than for daily rates and thus we tested the SEM to $J_{1.6}$ time series within NPF events. It showed out that SEM could approximate adequately the quickly varying $J_{1.6}$ data with sulphuric acid, ammonia, relative humidity, condensation sink, ozone and NOx concentrations as model variables.
We also studied the effects of the same predictors in SEM on the growth rate of the newly formed particles. It seems that sulphuric acid has a high contribution to growth rates of smallest particles but the effect of ammonia is low. Notable is that the ammonia concentration in SPC is relatively high as the station is in the most populated area of Italy and in the middle of area with intensive agricultural activities. It is possible that the ammonia concentration is always high enough to contribute to the NPF or subsequent growth processes and thus relatively small changes in ammonia concentration detected within the measurement campaign do not cause notable changes in measured $J_{1,6}$ or GR.

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OXIDIZED ORGANIC COMPOUNDS IN ATMOSPHERIC CLUSTERING

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Keywords: QUANTUM CHEMISTRY, CLUSTER FORMATION, ORGANIC MOLECULES

INTRODUCTION

Atmospheric aerosol particles are known to affect human health, radiation balance and atmospheric chemistry. Large fractions of the aerosol particles have been estimated to originate from atmospheric gas-to-particle phase transition. However, molecular-level formation mechanisms of atmospheric aerosol particles are still uncertain. Sulfuric acid is a key compound in the atmospheric particle formation, but it cannot alone explain the observed new-particle formation. Oxidized organic compounds have been shown to participate in the first steps of new-particle formation (Ehn, 2014).

STATE-OF-THE-ART QUANTUM CHEMICAL APPROACH

Density functional theory even with a small basis set yields good geometries and frequencies (Myllys, 2016a). In contrast, binding energies are very sensitive on the applied level of theory. To reach chemical accuracy in Gibbs free energies even for large clusters, we have utilized the domain-based local pair natural orbital coupled cluster (DLPNO–CCSD(T)) method (Riplinger, 2013). Benchmark calculations have shown that DLPNO results are close to the accuracy of canonical CCSD(T) with a significant gain in computational cost (Myllys, 2016b). In the results presented here, we have applied M06–2X, PW91, and \(\omega\)B97X–D functionals with 6–31++G** basis set for geometries and frequencies, and DLPNO–CCSD(T)/def2-QZVPP level of theory for single point energies.

ORGANIC PEROXYACID COMPOUNDS

The most commonly used precursor for studying biogenic secondary organic aerosols is \(\alpha\)-pinene \(\text{C}_{10}\text{H}_{16}\). Its autoxidation processes have not yet been fully resolved, but it is believed to produce compounds involving various carbonyl and hydrogen peroxide groups with oxygen-to-carbon ratios above 1. The formation of highly oxidized diperoxy acid compounds with additional keto and hydroperoxy substituents are reported from cyclohexene autoxidation (Rissanen, 2014). As a proxy for monoterpenic oxidation products, we have evaluated the potential of ketodiperoxy acid \(\text{C}_{6}\text{H}_{8}\text{O}_{7}\) to enhance sulfuric acid induced new-particle formation (see Figure 1). Our calculations identify that \(\text{C}_{6}\text{H}_{8}\text{O}_{7}\) interacts very weakly with itself and with sulfuric acid (Elm, 2015). This is due to the intramolecular hydrogen bonds of ketodiperoxy acid monomer structure, which stabilize the isolated molecule with respect to its clusters.

Figure 1. The structure of \(\alpha\)-pinene, where its cyclohexene structure is marked in pink (left) and \(\text{C}_{6}\text{H}_{8}\text{O}_{7}\) ketodiperoxy acid (right).
We have also investigated the stabilizing effect of water, ammonia, and dimethylamine on the clustering of sulfuric acid and ketodiperoxy acid. We found that the presence of water, ammonia, or dimethylamine enhances the molecular interaction between C₆H₈O₇ and H₂SO₄ compounds. However, the reaction free energies are only slightly negative, meaning that C₆H₈O₇ is likely to evaporate rapidly. The weak clustering ability of the peroxyacid compounds is due to the lack of strong hydrogen-bond acceptors. We concluded that autoxidation products consisting mainly of peroxyacid, hydroperoxide, and carbonyl groups cannot have an important role in the first steps of new-particle formation (Elm, 2016). The oxygen-to-carbon ratio alone cannot be used as a proxy for the volatility of oxidized organic compounds and hence their potential to enhance cluster formation. Multi-carboxylic acids are better candidates to participate in atmospheric clustering, since they are able to form stronger intermolecular hydrogen bonds (Elm, 2017a).

MULTI-CARBOXYLIC ACIDS

We have studied the molecular interactions between 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA, oxidation product of α-pinene) and sulfuric acid. The formation of the (MBTCA)(H₂SO₄) complex occurs by forming three hydrogen bonds, for which the reaction free energy is ~6.2 kcal/mol. This means that the formation of the sulfuric acid–MBTCA heterodimer is more favorable than either of the sulfuric acid or MBTCA homodimers (Elm, 2017b).

![Figure 2. Molecular structures of (MBTCA)(H₂SO₄) (left) and (MBTCA)₂ (right) clusters. Color coding: C=brown, O=red, S=yellow, and H=white.](image)

Clusters consisting of 2–3 MBTCA and 2–3 sulfuric acid molecules are particularly stable. However, cluster kinetics calculations showed that the cluster growth is limited by a weak formation of the largest sulfuric acid–MBTCA clusters. We have investigated the ability of bisulfate, ammonium, and ammonia to enhance cluster formation and growth by decreasing the overall evaporation rates of the clusters containing sulfuric acid and multi-carboxylic acids. The presence of ions enhances the first steps of two-component cluster formation. Bisulfate stimulates the clustering through the addition of sulfuric acid, whereas ammonium through the addition of organic acids. At atmospheric conditions, however, further cluster growth is limited due to the weak interaction and fast evaporation of the larger three-component clusters (see Figure 3). Bisulfate increases the evaporation rates of the three-component clusters due to the very high stability of two-component sulfuric acid–bisulfate clusters. It is very unlikely that organic multi-carboxylic acids and sulfuric acid, even together with bisulfate, ammonia, or ammonium can drive new-particle formation via clustering mechanisms (Myllys, 2017a).
Figure 3. Overall evaporation rates $\Sigma \gamma$ (sum over all decomposition processes) for MBTCA clusters at 273.15 K.

CHEMICAL REACTIONS AND STRONG BASES

We have demonstrated that non-basic organic compounds are unlikely to have a strongly enhancing role in the initial steps of sulfuric acid driven new-particle formation in atmospheric conditions. However, experimental studies have shown that oxidized organic compounds participate in the initial steps of new-particle formation. Due to the disagreement between theoretical and experimental findings, some other mechanisms or compounds are needed to explain the experiments.

One possible reason for the discrepancy between experimental and theoretical results might be the formation of covalently-bound dimers or organosulfates. The formed dimer or organosulfate products very likely have a lower saturation vapor pressure than the reacting monomers due to a higher molecular mass and a larger number of functional groups. We have showed that these clusters would be more stable against evaporation; therefore, cluster-phase reactions might play a significant role in atmospheric new-particle formation and growth (Hirvonen, 2017).

Furthermore, we have demonstrated that not only the atmospheric abundance but also the basicity and ability to form hydrogen bonds are important when estimating the ability of bases to form stable clusters (Xie, 2017). For instance, guanidine (a normal product of protein metabolism) binds with sulfuric acid four times stronger than dimethylamine, and thus even with a low concentration, it is able to enhance new-particle formation (Myllys, 2017b). Figure 4 presents the mesh-like structure of very stable $(\text{H}_2\text{SO}_4)_{4}(\text{guanidine})_{4}$ cluster. Due to a high stability against evaporation, sulfuric acid–guanidine clusters
could act as seeds for further growth via the uptake of other vapor molecules such as oxidized organic compounds.

Figure 4. Molecular structure of $(\text{sulfuric acid})_4(\text{guanidine})_4$ cluster.

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REFERENCES


ORGANIC SOIL IS A SIGNIFICANT YEAR-AROUND SOURCE OF VOLATILE ORGANIC COMPOUNDS

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INTRODUCTION

Boreal forest floor contributes from few percent to ten percent of the boreal forest VOC exchange depending on the season (Aaltonen et al., 2013), by emitting oxygenated VOCs, isoprene and monoterpenes, but also highly reactive sesquiterpenes (Mäki et al., 2017). Organic soil is expected to be a significant VOC source due to high organic carbon (SOC) content (Wiesmeier et al., 2014; Ostrowska and Grazyńska, 2015) and vegetative litter, which contains easily decomposable substrates for microbial processes. Warming can cause 90% increase on VOC emissions from Arctic plants (Kramshøj et al., 2016), but warming can also accelerated VOC synthesis through the decomposition processes, as microbial enzyme activity is driven by soil temperature and water content (Davidson et al., 2006). Wintertime VOC concentrations in soil and snow can be relatively high (Aaltonen et al., 2012) due to microbial decomposition processes. More understanding is needed about how different soil processes and soil components contribute to VOC formation (Leff and Fierer, 2008; Gray et al., 2010). Belowground VOC concentration measurements were conducted from the organic and from the mineral soil in a Boreal coniferous forest from the end of 2008 to end of 2011 (campaign 1) and in 2016 (campaign 2). The aim was to quantify the VOC compounds originating from boreal podsolized forest soil at different depths, as well as to connect VOC concentrations to the VOC emissions from boreal soil surface based on the following hypothesis: Organic soil and the top of mineral soil dominates the VOC emissions as organic soil is built by isoprenoid rich litter and fine roots and root-associated microbes are concentrated to the top mineral soil. Studies on belowground VOC concentrations are scarce (Lin et al., 2007), especially those which have been made in situ.

METHODS

The campaigns were performed in the boreal Scots pine stand (Pinus sylvestris) at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) station (61°51’N, 24°17’E, 180 m a.s.l). Soil above the homogeneous bedrock is Haplic podzol covered by vascular plants such as Vaccinium myrtillus L., Vaccinium vitis-idea L., Deschampsia flexuosa (L.) Trin., and Calluna vulgaris (L.) Hull., and mosses such as Pleurozium schreberi, Dicranum sp., and Hylocomium splendens (Aaltonen et al., 2011). The average C and N content is highest in organic soil layer (356 mg g⁻¹ and 13 mg g⁻¹) (Pumpanen et al. 2008).

Samples were collected by sucking air from the cylindrical hydrophobic gas collectors (4 cm in diameter, 12 cm long) installed into the soil using portable pumps, pumping air sample through Tenax TA–Carbopack-B adsorbent tubes (flow rate 100–150 ml min⁻¹) and by returning air back to collector. Set-up one was used from the end of 2008 to end of 2011 and set-up two in 2016 (Fig. 1). Disturbances to soil
profile were minimized by using a relatively small flow rate and circulating the air back to the collectors. Samplings were carried out in four 15 min periods with 15 min gaps between them to allow VOC concentrations equilibrate between the collectors and the soil during the break. Total sample volume was 6–9 L. Isoprenoid fluxes from forest floor were also measured during the second campaign with a dynamic enclosure chamber technique (Mäki et al., 2017).

**RESULTS AND DISCUSSION**

Noteworthy concentrations of monoterpenes were measured from the soil profile. Monoterpene concentrations were found to be highest in organic soil (Fig. 2a) and monoterpenes are probably released by decomposition of monoterpene rich litter (Hayward et al., 2001; Hellén et al., 2006; Leff & Fierer, 2008; Gray et al., 2010, Mäki et al., 2017), where decomposition processes are regulated by litter quantity and quality, climate and soil microbial populations (Prescott, 2000, Gray et al., 2010). Trees and perennial shrubs also emit monoterpenes (Smolander et al., 2006, Lin et al., 2007) and their roots are concentrated to the organic layer and the upper mineral soil. Sesquiterpene concentrations were found to be quite homogenous (Fig. 2b), indicating that sources are more stable and relatively independent from environmental factors. Sesquiterpenes are produced by endophytes (Bäck et al., 2010), decomposers (Bäck et al., 2010, Weikl et al., 2016) and ectomycorrhizal fungi (Ditengou et al., 2015).
Figure 2. Monoterpene (a) and sesquiterpene (b) concentrations (µg m⁻³) from the different soil horizons in 2016. Concentrations are means (S.E.) of the whole data. SQT1 was not identified.

Total monoterpene concentration median was highest in the organic soil (36 µg m⁻³), lower in the A-horizon (10 µg m⁻³) and smallest in lower horizons (B-horizon 4.2 µg m⁻³ and C-horizon 4.1 µg m⁻³). Belowground VOC sources were found to differ partly from the sources on soil surface as the fluxes were decoupled from the soil concentrations (Fig. 3). On soil surface, VOC probably originates from understorey vegetation and decomposing organic layer, humus (Hewitt and Street, 1992, Hanson et al.,...
Figure 3. The total a) isoprene, b) monoterpene, and c) sesquiterpene flux (µg m\(^{-2}\) h\(^{-1}\)) from forest floor and concentration (µg m\(^{-3}\)) from the each soil horizon from April to December in 2016.

1999, Janson et al., (1999), Aaltonen et al., 2011, Faubert et al., 2012, Rinnan et al., 2014). Monoterpene and sesquiterpene concentrations were measured throughout the year, but detectable isoprene concentrations were also found (Fig. 3), although isoprene is typically produced in photosynthetic tissues and emissions are strongly regulated by light (Monson et al., 1989, Delwiche et al., 1993, Sharkey et al., 1995). Isoprene can be produced by needle litter decomposition (Gray et al., 2010) and fungi (Bäck et al., 2010). Belowground sesquiterpene concentrations and forest floor fluxes were relatively high during spring (Fig 3). Sesquiterpene emissions from boreal shoots have been detected mainly in midsummer.
(Tarvainen et al., 2005, Hakola et al., 2006), which indirectly indicates that sesquiterpenes originate from decomposition processes and decaying substrates more than from vegetation. Highest monoterpane concentrations were measured in late summer, in October, and in December, similar to measured monoterpane fluxes which also peak in October (Hellén et al., 2006; Aaltonen et al., 2011, 2013, Mäki et al., 2017).

Belowground monoterpane and sesquiterpene concentrations were relatively high also under snowpack with possible icy layers and low temperatures, which hinders the diffusion, resulting accumulation of VOCs at snow-soil interface as well as in surface layers of soil. Concentrations were in the same order of magnitude as observed inside snowpack during winters (Aaltonen et al., 2012).

CONCLUSIONS

Boreal forest soil contained significant concentrations of monoterpenes and sesquiterpenes, when VOC concentrations were compared to the concentrations within a coniferous forest. Especially organic soil was found to be a significant VOC source, as expected, containing all the fresh, isoprenoid-rich litter. High VOC concentrations were also measured under snow cover, which can form physical barrier against diffusive transport and cause belowground accumulation of VOCs.

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LONG-TERM TRENDS IN PARTICLE SIZE-DISTRIBUTIONS AND NEW PARTICLE FORMATION OBSERVED AT SAN PIETRO CAPOFIUME, ITALY

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Keywords: particle number size-distributions, particle formation and growth, long-term trends.

INTRODUCTION

Atmospheric aerosols have a large impact on air quality, human health and even the global climate. One of the largest uncertainties related to climate change is the magnitude of the cooling effect of aerosols that counteracts the warming caused by greenhouse gases (IPCC, 2013). Both the aerosol number concentration and their size have influence on the climatic effects of aerosols (direct and indirect). Formation and growth of secondary aerosol particles is a major source of atmospheric aerosols (Merikanto et al., 2009), and has been a subject of active research during the past two decades. However, only few long-term datasets (over 10 years of measurements) of atmospheric new particle formation (NPF) exist. Observations in the Finnish boreal forest and at two Arctic sites in Finnish Lapland indicate very small changes in NPF over the past twenty years (Asmi et al., 2011; Kyrö et al., 2014; Nieminen et al., 2014), whereas in Central Europe a clear decrease in NPF occurrence has been reported (Hamed et al., 2010).

MATERIAL AND METHODS

In this work, we have characterized the trends in aerosol number size distributions and in NPF characteristics at the San Pietro Capofiume meteorological station located in Po Valley region, Northern Italy. The number size distributions of 3–630 nm particles have been measured at the station continuously since March 2002 with a twin-DMPS setup. The station is influenced by emissions of local anthropogenic pollutants (such as SO₂) as well as long-range transport from Central and Eastern Europe (Sogacheva et al., 2007), and thus can provide important information on the impact of anthropogenic activity on aerosol size-distributions and atmospheric NPF.

The particle number size distribution data was classified into NPF event, non-event and undefined days according to the guidelines presented by Kulmala et al. (2012). To quantify the NPF events, the formation rates of nucleation mode particles (defined here as particles of 3–25 nm in diameter) were calculated based on the measured number size-distribution data, taking into account the losses due to coagulation and the condensational growth of particles out from the nucleation mode. The particle growth rates were calculated by fitting log-normal modes to the measured size-distribution data and following the time evolution of the geometric mean size of the fitted nucleation mode.

To quantify the trends in particle concentrations, we have used two methods. The first method fits the concentration time series as a sum of constant linear trend and seasonally varying component, and the statistical significance of the fitted trend is estimated by performing the fitting multiple times with bootstrap sampling. The second method is based on a Dynamic Linear Model (DLM; see e.g. Durbin and Koopman, 2012). With this method we effectively decompose the particle number concentration timeseries into its basic components, such as the level, trend, seasonality, and noise. These components are
allowed to change as functions of time, and the magnitude of this change is modelled and estimated (Laine et al., 2014; Mikkonen et al., 2015).

RESULTS AND DISCUSSION

Figure 1a shows the daily averaged number concentrations of nucleation, Aitken and accumulation mode particles measured from 2002 to 2017. Note that there is a longer break in the measurements from November 2010 until June 2011, during which time the twin-DMPS setup was repaired. Before this break, a statistically significant decreasing linear trends are observed in all three particle size ranges. The largest decrease (–10%/year) occurs in the nucleation mode particle concentration. After the measurement break, only the nucleation mode particle concentration shows a statistically significant trend (decreasing –4.9%/year). The results from the DLM method (Figure 1b) indicate that the change in the particle concentration trends has occurred in 2008–2009.

The particulate mass concentrations (PM$_{10}$ and PM$_{2.5}$) have also been reported to decrease throughout the Po Valley region, and it is attributed to decreases both in primary emissions and in precursors of secondary inorganic aerosol emissions mostly from vehicular traffic (Bigi and Ghermandi, 2016). However, unlike the change in the trends of the particle number concentrations after 2007–2008 seen in our study, the PM concentrations seem to have continued their decrease until at least 2014.

The annual frequency of NPF event occurrence did not show any clear trend, varying between 20% and 40% of the days in a year. Both the formation and growth rates of nucleation mode particles had a decreasing trend of –3%/year and –2%/year, respectively. This would indicate that even though the sink for the newly formed particles has decreased (due to decrease in PM concentrations), a simultaneous decrease in precursor vapour emissions (sulphur dioxide, ammonia, amines, organics) has also occurred.

Figure 1. a) The measured daily mean number concentrations of nucleation (shown with blue datapoints), Aitken (magenta) and accumulation mode (black) particles together with their linear trends (shown with solid lines); b) the trends (expressed as rate of change per year, and smoothed with 30-day moving average filter) obtained from the Dynamic Linear Model. The time period of the maintenance break of the twin-DMPS instrument (November 2010 – June 2011) is omitted from the DLM results in panel b.
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REFERENCES


INTRODUCTION

Atmospheric aerosol are tiny particles in the atmosphere that are not distributed uniformly, and their size and composition vary in time and place. Most often elevated aerosol layers originate from the boundary layer (BL), where aerosols are emitted or formed. When the BL becomes suppressed during the sunset, aerosols remain in the residual layer and next morning they might not be mixed to the newly formed BL, but carried to the free troposphere. Convective motion can also transport aerosols from the BL to the free troposphere. In the free troposphere higher horizontal wind speeds transport aerosols to long distances, while smaller vertical velocities can also influence the aerosol flow. Wet deposition and evaporation to the gas phase are the main removal mechanisms that affect aerosols there. Some aerosol layers can also mix into the BL after several days of being aloft.

Understanding the vertical distribution of aerosols is important for determining the aerosol direct and indirect radiative forcing (Haywood and Ramaswamy, 1998). The aims of this work were to explore the BL and aerosol layers aloft in the rural environment, in order to connect them with backward trajectories to their source regions, to trace an exchange between the BL and free troposphere and to define processes that take place on the interface of neighboring layers. The combination of the lidar measurement, in situ measurements and back trajectories provide some information to answer these questions.

METHODS AND DATA

A High Spectral Resolution Lidar (HSRL, Shipley et al., 1983) was deployed in Hyytiälä from March to September 2014 as a part of the US DoE ARM (Atmospheric Radiation Measurement) mobile facility during the BAECC (Biogenic Aerosols – Effects on Cloud and Climate) Campaign. HSRL measures aerosol backscatter cross section, extinction cross section and depolarization with 1 second resolution at 532 nm. Cessna airborne campaigns took place in April and September 2014 during the operational time of HSRL. The flight tracks were above Hyytiälä at altitudes below 4 km and at a quite low speed (<200 km/h), which allowed measurements with good temporal and spatial resolution. A Cessna FR172F aircraft was modified to carry several instruments including a Scanning Mobility Particle Sizer (SMPS) and Optical Particle Sizer (OPS). SMPS has a temporal resolution of 2 min and measured particle sizes from 0.1 to 0.23 µm, while OPS has a 10 sec resolution and measuring particle sizes from 0.3 to 9 µm.

RESULTS

Period of three sequential days during 8 to 10 April was chosen for the case study. These days were all typical clear sky days with air masses coming from the north and new particle formation happening at the ground, which was detected at the SMEAR II station in Hyytiälä. Six flights in total were performed by Cessna during these days: one morning (between 9 and 12) and one afternoon flight (between 14 and 17)
each day. Figure 1 shows HSRL backscatter cross section coefficient for chosen case study, where evolution and development of different layers can be seen. Several layers can be identified in Fig. 1: the lowest layer corresponds to a well-mixed boundary layer that reaches up to 1500 m during the day, then there is a middle layer at 1200-1700 m, followed by an upper layer that stretches from around 1800 m to 3500 m. Profiles of relative humidity (RH) measured by the airborne humidity sensor and radiosonde support these layers identification (not shown on the graph).

Figure 1. HSRL backscatter cross section coefficient for chosen case study days: 8-10 April. The well-mixed boundary layer can be recognized by high values and other layers boundaries are seen from the gradient.

Figure 2 shows aerosol size distribution that was combined from the measurements of the SMPS and OPS for the afternoon flight during 9 April. The altitude of the Cessna flight is also displayed in the figure with pink colour. A strong gradient in the concentrations indicate a border between the BL and elevated layers. The highest concentration of all sizes of particles were detected in the BL. As the new particle formation event happened earlier that day, the concentration of nucleation and Aitken mode particles were very high compared to other modes. It is more difficult to differentiate between the middle and upper layers. During this day, the middle layer, seen from the HSRL, was thin and could contain only one or two airborne measurements, as two minutes of flight account for approximately 200 m of ascent. The middle layer was dominated by the particles between 0.1 and 0.6 µm. In the upper layer Particle concentrations in the upper layer were smaller in all size ranges, except for the Aitken mode particles, that have a bit higher concentration than in the middle layer. Nucleation mode particles were also detected at several heights in the upper layer. As these heights were not connected to the BL, these nucleation mode particles could be formed directly in the upper layer.

HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model, http://ready.arl.noaa.gov/HYSPLIT.php, Draxler and Hess, 1998) backward trajectories were calculated for every 50 m in altitude, and showed that the BL and the upper layer had slightly different origins. For the last 24 hours before arriving to the station, back trajectories were coming from the north, but before that air masses of the upper layer came from Greenland, whereas air masses of the BL arrived from the Barents Sea. Air masses of the upper layer had been in contact with the surface three days before, thus they could still carry the Aitken mode particles that they have collected there, that were not able to grow to bigger sizes.
Figure 2. Combined aerosol size distributions, measured by airborne SMPS and OPS, for the afternoon flight during 9 April. Pink line represent Cessna flight altitude.

CONCLUSIONS

We observed several elevated aerosol layers during the case study of three sequential days. The highest particle concentration all size ranges was found predominantly in the BL. The shape of the size distribution in the upper layer was often similar to the BL but with overall lower concentrations due to dilution of particles into a large volume of air. Moreover, variability in the number concentrations was the lowest in the BL due to turbulent mixing, and there were more variability in the elevated layers. 96-hours back trajectories for every 50 m for the altitudes from 0 to 4 km showed difference in the origin of the air masses. Origin of the air masses, as well as mixing and deposition, affect aerosol size distribution in different layers. Furthermore, we compared aerosol size distribution in the elevated layers during three consequent days and observed that there was almost no mixing of particles with the middle layer, as concentrations remained similar for all examined days, thus nucleation mode particles, that we observed in these layers, could have been formed in these layers.

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ACTIVE SITES IN HETEROGENEOUS NUCLEATION OF ICE

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Keywords: ICE NUCLEATION, SIMULATION, MOLECULAR DYNAMICS.

INTRODUCTION

Understanding the way in which ice forms is of great importance to many fields of science. Pure water droplets in the atmosphere can remain in the liquid phase to nearly -40 C. Crystallization of ice in the atmosphere therefore typically occurs in the presence of aerosol particles, such as mineral dust, soot or organic particles. These ice nucleating particles (INPs) trigger heterogeneous ice nucleation at clearly higher temperatures. Therefore, a better understanding of how the various types of aerosol particles present in the atmosphere affect ice nucleation (IN) in clouds would be an important advance in the field of atmospheric science.

Experiments have shown in great detail what is the IN activity of different types of compounds, and recently also clarified the importance of small surface features such as surface defects. The molecular-scale processes responsible for ice nucleation are still not well known, however, and difficulties in atomic-scale characterization of complex, imperfect surfaces means that a full understanding of these processes from solely experimental evidence is still a distant goal. In recent years, several computational studies have been published on heterogeneous ice nucleation, advancing our understanding of the details of ice nucleation for example on kaolinite, graphite, feldspars and silver iodide.

METHODS

We are utilizing an atomistic model of ice crystal formation comprising of a continuum of methods from density functional theory (DFT) to large-scale classical molecular dynamics (MD). We are looking at kinetic and thermodynamic factors controlling nucleation at different conditions and in the presence of different surfaces with varying lattice match with ice, representing aerosol particles.

To capture the details of the rare stochastic events of ice nucleation, it is necessary to simulate relatively large systems over long time scales, and therefore classical interaction potentials are used. We utilize the TIP4P/2005 model for water (Abascal and Vega, 2005), as this rigid point charge all-atom model has been shown to reproduce the water phase diagram well and is widely used to study water-ice phase transitions, as well as a computationally cheaper monatomic water model (Molinero and Moore, 2009). Unbiased MD is an ideal method to study physical pathways of ice formation from disordered water requiring collective molecular movement. We employ the DL\_POLY\_4 (Todorov et al., 2006) and LAMMPS (Plimpton, 1995) codes for parallel MD simulations, where a system including a surface immersed in water is cooled continuously below the melting point over tens of nanoseconds of simulation time and crystallization is followed. Also isothermal simulations are utilized, and we have investigated different nucleation modes including immersion-, contact- and deposition nucleation. We are simulating both ideal test systems with a suitable lattice match, surface corrugation, water-surface interactions, and realistic materials, feldspar and silver iodide, that are experimentally found to be active in heterogeneous nucleation, and we show what factors are affecting the nucleation activity.

In addition to studying nucleation dynamics with MD, we are looking at accurate energetics and parameterizing classical interaction potentials between water molecules and surfaces with quantum chemical DFT, utilizing the ORCA code (Neese, 2012) with BP86 functional with D3BJ dispersion.
Comparison of water layer adsorption on SiO$_2$ and graphite versus on K-feldspar is helping us understand the difference in nucleation activity between these materials. We are also utilizing DFT simulations to study water adsorption on hydroxylated graphene, a model for weathered black carbon.

CONCLUSIONS

A surface with a good lattice match with hexagonal ice nucleates ice effectively at MD time scales (in the order of 10-100 nanoseconds) in immersion mode nucleation, which is regarded as the most important nucleation mode for ice formation in clouds in the atmosphere. Results from mW potential simulations show that surface geometry alone can explain the high nucleation activity of AgI, whereas K-feldspar, which is considered one of the most important ice nucleation agents in the atmosphere, shows very weak activity in mW simulations, without considering the real surface chemistry or defects of the material. We have further studied the ice nucleation activity of feldspars, focusing especially on the importance of the effect of feldspar microstructure and different crystallographic faces of feldspar (see Fig. 1), which recent experiments have shown to be responsible for IN activity of feldspars (Kiselev et al., 2017). Feldspars are most likely the dominant ice nucleating agent in the atmosphere. For these simulations, the water-surface interactions were parameterized with quantum mechanical methods. We have also started the research on possible candidates for optimized (artificial) ice nucleating particles, and we are preparing the experimental realization of these ideas.

Figure 1. Orthoclase (K-feldspar) (100) surface effectively nucleates ice. Our MD simulations shows that ice grows with the prism face aligned with the surface, in contrast to most other surfaces.

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REFERENCES

CAN A PATHOGENIC FUNGUS DISTURB THE WATER TRANSPORT VIA SURFACE TENSION IN NORWAY SPRUCE?

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Keywords: ENDOCONIDIOPHORA POLONICA, PICEA ABIES, WATER TRANSPORT, SURFACE TENSION, RESIN.

INTRODUCTION

Linking fungal infection to physics behind tree physiology is exceptional in the field of plant pathology and plant physiology, and provides an insight to the reasons causing tree mortality. *Endoconidiophora polonica* (Ascomycota) is a pathogenic blue stain fungus vectored mainly by the spruce bark beetle (*Ips typographus*) (Christiansen, 1985; Christiansen and Solheim 1990). Climate change likely decreases tree vitality e.g. by more frequent storm damages in boreal forests and thus predisposes trees to insects and pathogenic fungi attacks (e.g. Seidl et al., 2011). *Endoconidiophora* and other pathogens may cause a serious drought stress in living trees by disrupting the water and solute transport between the roots and the canopy (Jactel et al., 2012). The studied fungus infection (*E. polonica*) may hinder water transport in trees by mechanical blocking in the water transport route (e.g. Kuroda, 2005; Yadeta and Thomma, 2014) or by decreased surface tension of water in xylem, which increases the vulnerability of tree water transport to hydraulic disturbances (Tyree and Sperry, 1989). Though both the fungus infection and water transport are much studied the mechanisms behind the tree weakening process during infection remain unknown.

METHODS

The study was conducted at the Viikki campus greenhouses. The cloned saplings of Norway spruce (*Picea abies*) were potted and brought from the Nursery of Natural Resources Institute Finland. The saplings (about 1.2 m long) were divided in three treatment groups: inoculated trees (10 per clone), wounded trees (10 per clone) and intact control trees (5 per clone). The first group was inoculated with agar-grown fungal mycelium in the beginning of June 2016. The second group was mock-inoculated (later referred as wounded control). The third group was left intact.

Tree water relations, including hydraulic conductivity, hydraulic conductance and surface tension of xylem sap were measured with resin pressure and volatile organic compounds (VOC) from Norway spruce saplings. Tree water relations were monitored with whole tree level hydraulic conductance measurements that were carried out by measuring the transpiration and the stem water potential. Hydraulic conductance was calculated to be the ratio between the transpiration rate and the stem water potential. The transpiration was measured weighing the water loss of the saplings whereas the water potential was measured from the needles with a pressure chamber (PMS Instrument Company, Albany, US). The water column breaks, i.e. embolism, and therefore the proceeding of the fungus infection was monitored with Ultra acoustic emission (UAE) sensors (R15a, Physical acoustics corporation, NJ, US). Plant material was sampled every week throughout the summer. Once a tree stem was cut off, the conductivity of the stem was measured by flow of water pushed through sampled tree pieces with c. 0.1 bar over pressure (Sperry et al. 1988). The first water drops coming through these pieces were used for the surface tension measurements. Surface tension was measured using a capillary rise technique with calibrated capillary tubes (Vanhanen et al. 2008). Additionally, the relative water content was measured from a separate stem piece.
Resin pressure in the stems was measured in order to observe the constitutive and inducible defense reactions provoked by the inoculations, and to examine the effect of decreasing water potential, hydraulic conductance and conductivity on the resin dynamics. Resin pressure measurements were conducted with lightweight differential pressure sensors (Model MPX5250, NXP Semiconductors, Eindhoven, Netherlands, figure 1), which were tailored for this study, and were installed on small wounds (diameter about 1.5 mm) punched through the tree stem phloem. Pressure data was collected every ten seconds throughout the experiment with few gaps due to re-installation or malfunction of sensors.

VOC (volatile organic compound) measurements were done to monitor if fungal infestation causes qualitative or quantitative changes in the emissions from tree stems. Cartridge samples were collected from small enclosures attached around the stems every other week throughout the experiment.

RESULTS

The xylem hydraulic conductivity and surface tension of infected trees were lowered compared to control trees (Fig. 1 and 2). The hydraulic conductivity of infected trees decreased with the decreasing surface tension (Fig. 1). The hydraulic conductance, that was the relation of tree transpiration and water potential, was not different between the treatments. The resin pressure showed larger variation in infected trees whereas the VOC emissions indicated yet unclear response to infection.

Figure 1. Hydraulic conductivity and surface tension of clones 64 and 1510. The abbreviation “cp” stands for the infected trees.
CONCLUSIONS

Our results suggest that the mechanisms how *E. polonica* overcomes the defense of Norway spruce are related to lowered surface tension and increased vulnerability to cavitation in xylem due to the infection. A lower surface tension of tree sap, as caused by increased concentrations of organic surfactants, decrease the ability of water columns to withstand water stress. Therefore, water stress conditions most probably help the progress of tree weakening during *E. polonica* infection.

REFERENCES


FATE OF SULFURIC ACID CLUSTERS INSIDE THE API-TOF

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Keywords: API-TOF, CLUSTER, SULFURIC ACID, DMA.

INTRODUCTION

Chemical Ionization Atmospheric Pressure interface Time Of Flight mass spectrometer (CI-API-TOF) has revolutionized the study of atmospheric new particle formation. This instrument is able to detect small clusters, which are involved in the first stages of new particle formation, even at environmental low concentration. It can give the elemental composition of clusters and an estimate of their concentration, if the instrument is carefully calibrated. Moreover, the development of highly selective chemical ionization techniques (e.g. using nitrate as reagent ion) can allow the selective ionization of interested clusters, eliminating the interferences from all other molecules and clusters present in the atmosphere (Jokinen et al., 2012). Although the use of the CI-API-TOF is exponentially grown in the last years, a systematic study on the fate of atmospheric clusters inside the instrument has not been carried out until now. It has been reported that clusters can undergo transformation inside the instrument, in particular the charging process, the low pressure and also energetic collisions with neutral molecules can affect the molecular composition of clusters (Kürten et al., 2014). This hypothesis is also supported by computational studies, indeed, it has been shown that theoretical models predict a higher cluster concentration than the measured concentration (Olenius et al., 2013). This discrepancy has been attributed to the cluster fragmentation process inside the instrument, which is not taken into account.

Sulfuric acid is a key species in new particle formation, and together with ammonia and amines, it seems to be involved in many nucleation processes (Vehkamäki and Riipinen, 2012). In this study, we investigated the fate of sulfuric acid clusters inside the API-TOF to determine the factors and the conditions that lead to transformation of clusters inside the instrument. To reach our goals we combined a high resolution Differential Mobility Analyzer (DMA) with the API-TOF. The DMA classifies charged particles (and clusters) as a function of their electrical mobility, hence with this instrument is possible to measure the clusters size and separate them based on their size. Combining these two instruments, we can select only one cluster size and inject it into the mass spectrometer. In this way, we can have the powerful combination between a separation and a characterization technique. Injecting into the API-TOF only a mono-mobile size ions distribution it is easier to understand the fate of clusters inside the instrument because only one kind of clusters is studied at a time.

METHODS

The experiments were carried out in the laboratory and sulfuric acid (H2SO4) clusters were produced by ElectroSpray Ionization (ESI). Different concentrations and solvents were tested to obtain a suitable cluster size distribution. Ions generated by ESI are guided into the DMA where a mono-mobile size ions distribution was selected and injected into the mass spectrometer. A schematic representation of the ESI-DMA-API-TOF is shown in Figure 1. The ions are guided inside the atmospheric pressure interface (API) through a series of three vacuum chambers before arriving to the time-of-flight detector. The pressure decreases between successive chambers until arriving to 10^-6 mbar in the mass spectrometer. In the first two chambers (SSQ and BSQ) the ions are guided through quadrupoles (Quad1 and Quad2), while in the last chamber (PB) several lenses focus the ions. In total, 27 voltages and 2 radio frequencies are applied to
APi-TOF, most of which can be changed to optimize the results as a function of the specific application of the instrument. The tuning of the APi-TOF was systematically changed to study its impact of cluster fragmentation inside the API section. In particular, in this work we selected sulfuric acid trimer cluster through the DMA and we evaluated the effects of the voltages applied to SSB and BSQ on its fragmentation.

![Figure 1. Schematic representation of the ESI-DMA-API-TOF and possible fate of atmospheric clusters inside the instrument.](image)

CONCLUSIONS

Negatively charged sulfuric acid trimer cluster \(((\text{H}_2\text{SO}_4)_2\text{HSO}_4^-)\) can undergo fragmentation following three pathways:

\[
\begin{align*}
(\text{H}_2\text{SO}_4)_2\text{HSO}_4^- &\rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_3\text{HSO}_4^- \quad (\text{Eq. 1}) \\
(\text{H}_2\text{SO}_4)_2\text{HSO}_4^- &\rightarrow 2 \text{H}_2\text{SO}_4 + \text{HSO}_4^- \quad (\text{Eq. 2}) \\
(\text{H}_2\text{SO}_4)_2\text{HSO}_4^- &\rightarrow (\text{H}_2\text{SO}_4)_2 + \text{HSO}_4^- \quad (\text{Eq. 3})
\end{align*}
\]

Theoretical calculations show that the first one (Eq.1) is the most favorable at room temperature as confirmed also by experimental data. In this study, we demonstrate that clusters are strongly affected by the tuning of the instrument, indeed fragmentation of \((\text{H}_2\text{SO}_4)_2\text{HSO}_4^-\) in sulfuric acid dimer \((\text{H}_2\text{SO}_4\text{HSO}_4^-)\) and monomer \((\text{H}_2\text{SO}_4)\) is always observed. The voltages applied to the first chamber (SSQ) haven’t a significant impact on sulfuric acid trimer fragmentation and can be varied in a large range (over 30 Volts). An opposite trend is observed for the voltages applied to the second chamber (BSQ) where a change of few voltages can lead to complete fragmentation of the clusters. In particular, the voltage difference between the SSQ and BSQ chamber seems to have an important impact on cluster fragmentation. Keeping the voltage difference \((\Delta V)\) as low as possible the fragmentation decreases, whereas the increase of \(\Delta V\) leads to higher fragmentation. In the SSQ due to the pressure (2 mbar) clusters are more effected by the fluid dynamics of the chamber rather that the electric field applied by the voltages. While in the second chamber cluster are strongly accelerated by electric field, this leads to energetic collisions with neutral molecules resulting in cluster fragmentation.

Moreover, we demonstrate that the tuning can significantly affect the sensibility of the instrument. For example, we showed that the voltages applied to the second quadrupole (Quad2) are crucial to allow ions to pass through the BSQ. To detect negatively charged clusters a positive \(\Delta V\) between Q2 front and back is needed, while a negative \(\Delta V\) is required to analyze positive ions.
This preliminary study allows to better understand the fate of clusters inside the APi-TOF and it could be useful to correctly determinate the concentration and composition of sulfuric acid-amine clusters in the atmosphere. Moreover, it lays the bases for developing a theoretical model to describe and predict the fate of clusters inside the APi-TOF.

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REFERENCES


PARTICLE GROWTH RATES FROM NUCLEATION MODE TO CLOUD CONDENSATION NUCLEI SIZES

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Keywords: PARTICLE GROWTH RATE, AITKEN MODE, ACCUMULATION MODE.

INTRODUCTION

Predicting the future climate requires precise knowledge on interactions of different factors in the atmosphere. Currently, the direct and indirect effects of aerosols form the largest uncertainties in climate predictions (Stocker et al. 2013). Indirect effects refer to the ability of aerosols to act as cloud condensation nuclei (CCN). For the particles to act as CCN, their diameters have to be at least 50-150 nm and their chemical composition and meteorological conditions have to favour cloud droplet formation (Kerminen et al. 2012). A major fraction of CCN are formed through gas to particle conversion (Merikanto et al. 2009; Paasonen et al. 2013; Peng et al. 2014). The vapours that condense on aerosol particles, and thus form more particulate matter by growing them, are typically oxidised volatile organic compounds (VOC). These vapours can originate from biogenic sources, such as emissions of plants (Hallquist et al. 2009).

If new particle formation (NPF) occurs as a regional scale event, the growth of the particles can be observed in one measurement point for several hours. In such cases, we can determine the growth rate (GR) of the particles. In most cases, the conditions are not homogeneous enough for the growth to continue from freshly nucleated particles up to CCN sizes directly. This is why there is little research done on the growth of the particles in sizes approaching the CCN size range.

We developed a new method that calculates growth rates automatically from size distribution data for all size ranges from 3 to 1000 nm. It takes into account all the data, not only times immediately after NPF events. This expands the amount of available data tremendously. Here, we use as an example growth rates calculated for data from Hytiälä, Finland and compare them to different variables presumably associated with NPF.

METHODS

Particle growth rates are traditionally calculated for nucleation mode particles ($d_p <25$ nm) during new particle formation (NPF) events (e.g. Nieminen et al. 2014). However, particle growth episodes can be observed also in larger size ranges and not following a NPF event observed at the measurement site. In order to obtain more knowledge on the growth, we developed a new method that calculates particle growth rates not only for the nucleation mode but also for Aitken (25 nm $<d_p<100$ nm) and accumulation modes ($d_p>100$ nm). The minimum length of a growth period, for which the growth rate (GR) is determined, is here set to be 5 hours. The method was developed using particle size distribution data measured with a Differential Mobility Particle Sizer (DMPS) in Hytiälä, Finland (Hari and Kulmala 2005). An example of a day with multiple determined growth episodes is depicted in Figure 1.
In order to explore how different factors affect the growth of the particles, several different variables have been compared to the growth rates. These variables include for example meteorological data, condensation sink (CS) formed by the existing particle population and concentrations of monoterpenes and their oxidants.

RESULTS AND DISCUSSION

The maximum of the observed growth rates increases as a function of size of the growing particles (Fig. 2). However, this effect is less clear for nucleation mode particles than for larger sizes. The size-dependency of the growth rates is presumably formed of two different factors. Firstly, in nucleation mode, the growth is mainly due to irreversible condensation of non-volatile compounds. Also, for nucleation mode particles, very small growth rates for as long as five hours would not be observable as the particles would be scavenged by the existing particle population instead of growing.

Secondly, in larger size ranges, the condensation of semi-volatile compounds and particle phase chemistry can increase the growth rate as a function of size. This is because semi-volatile compounds that normally have significant evaporation rates can react in the particle phase and form non-volatile compounds that will not evaporate. The amount of the products of these reactions is limited by the volume of the particles as shown in a modelling study by Apsokardu and Johnston (2017) for sub 100 nm particles. Condensation of the compounds on the particle surface, on the other hand, is limited by the surface area of the compounds. As the relationship of the particle volume and area increases linearly as a function of particle diameter, the growth rate can also increase linearly as a function of size (Apsokardu and Johnston 2017). This is in line with our results as the maximum observed growth rates increase as a function of size.

This hypothesis is supported by a laboratory study by Tu and Johnston (2017) that shows increasing amount of oligomers and decreasing oxygen to carbon ratio with increasing particle size. The importance of the effect of particle phase chemistry depends on the chemical compounds involved in the growth and meteorological conditions (Tu and Johnston 2017) and this is one of the reasons why the lower limit of the growth rates is less clear than the upper limit.

Other variables that we tested included ambient temperature and condensation sink. Between temperature and growth rates, a positive correlation was observed in different size bins below 100 nm. This is
presumably due to the temperature dependence of the VOCs emitted by the vegetation. We expected that increasing condensation sink, that is assumed to take up condensing vapours, would decrease the growth rates as the condensing vapours condense on larger surface. However, in our results the condensation sink did not have any decreasing effect on the growth rates even in temperature and size bins.

Figure 2. Growth rates as a function of the initial diameter of the growth episode. The colour indicates the mean temperature during the growth event. The data are from all seasons.

CONCLUSIONS

A new automatic method has been made for calculating the growth rates from size distribution data. It can be applied not only for nucleation mode but also for Aitken and accumulation modes. To our knowledge, this data set is the first to include the growth periods also not immediately following a NPF event.

Our data show that the maximum observed growth rate increases as a function of particle size in Aitken and accumulation modes. This size dependence of the growth rates can be explained by different factors affecting the growth in different size ranges. In nucleation mode, the particles grow mostly due to irreversible condensation of non-volatile compounds.

For Aitken mode, the condensation of semi-volatile vapours and particle phase chemistry starts to increase the growth rates. A positive correlation was observed between the growth rates and ambient temperature for nucleation and Aitken mode particles and this is assumed to be due to the temperature dependence of VOC emissions by plants.

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REFERENCES


FORMATION OF CONDENSIBLE VAPOURS FROM α-PINENE OXIDATION: EFFECT OF NOX ON EXPERIMENTALLY DERIVED VOLATILITY DISTRIBUTION

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Keywords: HOM, SOA, NOX, Volatility.

INTRODUCTION

Organic compounds are ubiquitous in atmospheric aerosol worldwide (Zhang et al., 2007). The majority of the organic aerosol is only formed in the atmosphere, through the conversion of gaseous volatile organic compounds (VOCs) into condensable forms through their oxidation (Jimenez et al., 2009). Aerosol formed in this way is called secondary organic aerosol (SOA). Despite intensive research over the past decades, there has been a mismatch between the modelled and measured SOA formation, with models underpredicting formed aerosol mass (Hallquist et al., 2009). One promising candidate to explain this underprediction is the recently found class of VOC oxidation products, highly oxygenated molecules (HOMs, Ehn et al., 2014). HOMs form rapidly in the oxidation of many VOCs, including monoterpenes, the most abundant group of VOCs emitted by boreal forests. Their volatility is expected to be low or extremely low based on their molecular formulae and assumed functional groups, and their contribution to aerosol formation. Still, direct determination of their exact volatility has remained a challenge. Here we present an experimental method for determining the volatilities of the HOMs, and apply it to the oxidation of α-pinene, an abundant monoterpene, with ozone. We then investigate how the addition of nitric oxide (NO), affects the volatility distribution of the products, as it offers a potential mechanism for anthropogenic activities influencing the formation of biogenic SOA.

METHODS

We performed experiments in a two-cubic metre Teflon chamber, operated in a continuous flow mode with the residence time of 50 minutes. We injected α-pinene into the chamber along with ozone. In addition, we could inject nitrogen dioxide (NO2) and photolyze it to NO using UV lights, inject ammonium sulfate (AS) seed particles, and control the relative humidity of the chamber. All experiments were conducted at the temperature of 298 K.

We measured the chamber air with a wide suite of both gas- and particle phase instrumentation. For the measurement of gas-phase HOMs, we used a chemical ionization atmospheric pressure interface time of flight mass spectrometer (CI-API-TOF, Jokinen et al., 2012), utilizing nitrate ion for the ionization. The instrument was equipped with a long time of flight analyser, providing superior mass resolution (up to 13 000 in the HOM mass range).

To study the volatility of HOMs, we started with only α-pinene and ozone being injected to the chamber. After the system had reached steady state, we started injecting AS seed particles into the chamber, providing more surface area for the HOMs to condense on. With low enough volatility, HOMs that condense onto seed particles or chamber walls will not evaporate back to the gas phase during the chamber residence time. In this case, their gas-phase concentration is determined by the steady state between their gas-phase production and irreversible condensation. Increasing the condensation rate by
introducing more surface area hence decreases their gas-phase concentration. Increasing the volatility of HOMs leads to increased evaporation rates, and with high enough volatility the HOMs will rapidly form an equilibrium between the gas and condensed phases. Addition of seed particles does not disturb this equilibrium. Hence, we can separate the HOMs according to their volatility based on the response of their gas-phase concentration to seed addition. Products that are unaffected by seed addition are of high volatility, and those affected much are of low volatility. This provides an experimental volatility scale, independent of any assumed structures or thermal stabilities. However, without further modelling and calculations, this scale is only relative: we know if one compound is more volatile than another, but do not know the exact volatility. This will be resolved in the near future by modelling efforts.

RESULTS

The volatility of HOMs generally decreases with increasing molar mass, as expected. However, this decrease is not monotonous, but depends on some properties of the compounds. Most notably, organic nitrates are of higher volatility compared to non-nitrates of similar mass. This can be explained by the fact that the nitrate group increases the molar mass of a compound a lot, while decreasing the volatility only moderately (Kroll et al., 2008). Addition of NO enhanced the formation of these relatively more volatile compounds, while suppressing the formation of low-volatility dimers. Hence it shifted the whole distribution of HOMs towards higher volatilities. Here we have presented relative volatilities. Further work is still needed to convert these to absolute numbers.

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REFERENCES

INTRODUCTION

Atmospheric concentration of the strong greenhouse gas methane (CH$_4$) is rising with an increased annual growth rate. Biosphere has an important role in the global CH$_4$ budget, but high uncertainties remain in the strength of its different sink and source components. Among the natural sources, the contribution of vegetation to the global CH$_4$ budget is the least well understood. Role of trees to the CH$_4$ budget of forest ecosystems has long been overlooked due to the perception that trees do not play a role in the CH$_4$ dynamics. Methanogenic Archaea were long considered as the sole CH$_4$ producing organisms, while new findings of aerobic CH$_4$ production in terrestrial vegetation and in fungi show our incomplete understanding of the CH$_4$ cycling processes. Enclosure measurements from trees reveal that trees can emit CH$_4$ and may substantially contribute to the net CH$_4$ exchange of forest ecosystems.

The main aim of MEMETRE project is to raise the process-based understanding of CH$_4$ exchange in boreal and temperate forests to the level where we can construct a sound process model for the soil-tree-atmosphere CH$_4$ exchange. We will achieve this by novel laboratory and field experiment focusing on newly identified processes, quantifying CH$_4$ fluxes, seasonal and daily variability and drivers of CH$_4$ at leaf-level, tree and ecosystem level. We synthesize the experimental work to build a process model including CH$_4$ exchange processes within trees and the soil, transport of CH$_4$ between the soil and the trees, and transport of CH$_4$ within the trees. The project will revolutionize our understanding of CH$_4$ flux dynamics in forest ecosystems. It will significantly narrow down the high uncertainties in boreal and temperate forests for their contribution to the global CH$_4$ budget.

The main scientific objectives of MEMETRE are:
1. To identify the roles of aerobic, fungal and methanogenic CH$_4$ production within trees, and the contribution of the transported CH$_4$ to the emissions of CH$_4$ from trees
2. To quantify CH$_4$ emission rates and their temporal patterns and to identify driving variables of CH$_4$ emissions from different processes, and describe them mathematically
3. To build a process model that includes aerobic and fungal CH$_4$ production and transport mechanisms

METHODS

The project has a strong experimental base necessary to obtain the process level information for the modelling. We use novel enclosure methods in laboratory and in field-scale to investigate gas exchange of tree seedlings and mature trees (Pihlatie et al., 2005; Pihlatie et al., 2013; Machacova et al., 2016), we utilize existing research infrastructure sites (e.g. ICOS) to guarantee state-of-the-art facilities for our CH$_4$ flux measurements. Simultaneously with the measurements, we construct a process-based model that includes 1) CH$_4$ production and consumption processes in the soil, 2) transport processes within the soil, from the soil to the tree, and within the tree, and 3) in-situ CH$_4$ production processes in trees. The aim is to produce a model that can be integrated to the global land surface models such as JSBACH (Reick et al., 2013).
The work of this project is divided into three closely related work packages (WP 1-3), as summarized in Fig. 1.

Figure 1. A schematic of the work packages of the project MEMETRE. All three work packages are interconnected and feedback to each other. WP1 quantifies the CH₄ fluxes and processes in the laboratory, WP2 quantifies the CH₄ fluxes, and connections to flux drivers in the field at different forest ecosystems, WP3 integrates the experimental work and theoretical understanding into mathematically described processes and a model combining CH₄ cycling processes and exchange between soil, trees and the atmosphere.

EXPECTED RESULTS

This project brings the understanding of CH₄ emissions from trees to a new level where the processes and the process drivers are identified and formulated into a process model of soil-tree-atmosphere CH₄ exchange. Novel and unique CH₄ flux measurements of undisturbed leaf-level and stem CH₄ fluxes from different tree species in boreal and temperate forests is foreseen to revolutionize our understanding of CH₄ flux dynamics in forest ecosystems. For the first time in the world, the short-term leaf-level CH₄ dynamics can be connected to the physiological activity of the trees, fluxes of other trace gases and a multitude of environmental parameters. The laboratory experiments will provide process level understanding of leaf-level CH₄ formation in tree in connection to biotic and abiotic drivers, as well as in-depth knowledge of fungal CH₄ formation in trees and the connection to methanotrophic activity. The project is synthesized in the soil-tree-atmosphere process model that combines the CH₄ exchange processes within trees, and between the soil, trees and the atmosphere. With the process model we can estimate the role of trees in the CH₄ budget of boreal and temperate forests. We aim that the model will also be incorporated to global land surface models such as JSBACH, eventually providing global estimates of CH₄ emissions from trees.
CONCLUSIONS

The biggest breakthrough of the project is that in the end we can answer the question: how much trees contribute to the CH$_4$ budget of boreal and temperate forest ecosystems. Our work will hence significantly narrow down the high uncertainties in boreal and temperate forests for their contribution to the global CH$_4$ budget.

ACKNOWLEDGEMENTS

This project will receive funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grant agreement No (757695), Academy of Finland Research Fellow project (294088), and Helsinki Institute of Life Sciences (HiLIFE Fellow grant). Also the Academy of Finland Center of Excellence programme (307331) is acknowledged.

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FLUORESCENCE ACROSS SPACE AND TIME (FAST) 2017: A MULTISCALE CAMPAIGN TO INTERLINK CHLOROPHYLL FLUORESCENCE AND THE SPRING RECOVERY OF BOREAL FORESTS


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Keywords: SOLAR-INDUCED FLUORESCENCE, MULTISCALE MEASUREMENTS, MULTIPLE SPECIES, LEAF-LEVEL, CANOPY-LEVEL, DRONES, SATELLITE DATA.
INTRODUCTION

Solar-induced chlorophyll fluorescence (SIF) is currently regarded as one of the most promising tools to track vegetation photosynthesis from space in the near future (Guanter et al. 2014; Sun et al. In Press). Increasing numbers of currently available and soon-to-be-launched satellite missions ensure that the spatial and temporal resolution of satellite SIF data will continue to improve. SIF is emitted by the photosynthetic apparatuses of higher plants nanoseconds after light absorption, conveying real-time and first-hand information on the performance of the photosynthetic machinery. Very importantly, a multitude of factors will also influence the spectral and radiometric properties of the SIF signal which need careful characterization and consideration when interpreting the data.

Upscaling our understanding of the fluorescence signal from short-term and leaf-level measurements to seasonal and satellite pixel-level measurements requires a comprehensive treatment of the spatial and temporal scales and factors involved therein. Although a number of recent activities have already started to shed some light into the factors that affect the spectrum and intensity of the SIF signal, these activities have been confined to a particular scale, for example, measurements of different spatial scales at a certain point in time, or measurements over time of a single spatial scale. We believe that simultaneous measurements across both space and time are required in order to successfully reveal the true impact of each factor and establish a true quantitative connection between leaf-level physiology and satellite pixel dynamics.

The goal of the FAST campaign (Fluorescence Across Space and Time) was to co-register the photosynthetic spring recovery of a boreal forest at multiple scales in order to evaluate how the relationship between SIF and photosynthesis changes from scale to scale (both in time and space) and what are the processes responsible for the relationships at each scale.

METHODS

The FAST campaign comprised a multidisciplinary group of collaborators from very diverse areas of expertise, covering a multitude of scales and providing expertise and access to a wide range of methods. The campaign took place in SMEAR-II Station in Southern Finland between February and July 2017. Measurements covered the three most significant tree species in the boreal forest around the station: Scots pine (*Pinus sylvestris*), Norway Spruce (*Picea Abies*) and Birch (*Betula pendula*); as well as the two most common ground species: Lingonberry (*Vaccinium vitis-idaea*) and Bilberry (*Vaccinium myrtillus*).

Spatially, we collected: a) leaf samples for molecular analysis of pigments and proteins; b) carried out leaf-level measurements of photosynthesis, carbonyl sulphide (COS), volatile organic emissions (VOCs), reflectance, transmittance, absorption and fluorescence spectra (see Abstract by Rajewicz et al.), photosystem II and photosystem I dynamics, C:N, specific leaf area, relative water content, and light environment across canopy positions; c) conducted canopy-level measurements of CO2, water, COS, and VOC fluxes, as well as spectral reflectance, SIF and fluorescence spectra (See Abstract by Atherton et al.); d) we also conducted vertical profiles of irradiance, radiance and SIF using a drone platform flying from 30m to 500m height over pure stands of birch, pine, and spruce as well as mixed forests. In addition we also measured the 3D structure of those stands with a terrestrial laser scanner which will be used for radiative transfer modelling (see Abstract by Weiwei et al.), finally e) we co-registered satellite pixel SIF data from NASA’s OCO-2 satellite which was set to target mode over SMEAR-II station during the campaign. See Figure 1 for some examples.

At the temporal scale, we combined continuous measurements of leaf and canopy level fluorescence, gas exchange, VOCs, COS with point acquisitions during a total of 10 intensive measuring points. UAV vertical profiles and successful OCO-2 satellite observations were carried out in three occasions only due to weather and logistic restrictions.
FUTURE STEPS

We successfully managed to co-register the optical, functional, and structural components of the spring recovery of a boreal forest. We are at present analysing the multiple datasets and continuing with the laboratory analysis. We expect that this dataset will not only serve to elucidate the processes that control the relationship between fluorescence and photosynthesis at different scales but also serve as reference testbed for testing and validating multiple models.

Figure 1. Examples of multiscale data and novel methods used during the FAST campaign. We collected leaf samples to quantify the seasonal changes in key photosynthetic proteins (Panel A) and leaf pigment contents. We used a new method to estimate total leaf absorption of leaves independently of their shape and morphology, leaves are hanged inside the sphere and measured before and after painting them black (Olascoaga et al. 2016) (Panel B). A novel dual field of view spectrometer (Piccolo Doppio) was used to measure canopy reflected radiance and incoming irradiance (sensor pointing up not visible in the picture) and retrieve the integrated SIF signal of all canopy components (Panel C). The same system was also used in a drone (Pannel E) to register SIF across multiple footprints and study how the signal scales up from the canopy (flights at 30m altitude) up to the stand and satellite pixel level (flights at 80, 200 and 500m altitude). Note the fields of view (shaded grey areas) of the two optical sensors for quasi-simultaneous irradiance (downwelling) and reflected radiance (upwelling) measurements. We also captured fish-eye images at the sampling points (Panel D) in order to characterize the role of the light environment in dictating the vertical variation in leaf optical traits within a plant canopy. At the largest scale, NASA’s OCO-2 satellite provided estimates of SIF over SMEAR-II area (Panel F) at a pixel resolution of 1x2 Km.

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REFERENCES


TOWARDS LONG-TERM TOTAL OH REACTIVITY MEASUREMENTS IN A BOREAL FOREST

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Keywords: hydroxyl radical (OH), OH reactivity, biogenic volatile organic compounds (BVOCs), seasonality

INTRODUCTION

The total hydroxyl radical (OH) reactivity is used to assess how exhaustive are measurements of individual compounds. The approach was introduced in the early 2000s by Kovacs and Brune (2001). The original method is based on direct measurement of OH decay by laser induced fluorescence (LIF) techniques. Later, a more affordable method based on measuring the concentration change of a tracer in zero air (all OH react with the tracer) and ambient air (competition for OH from compounds present in the sampled air) has been developed, namely the Comparative Reactivity Method (CRM, Sinha et al., 2008).

A new implementation of the CRM method has been developed and tested at the Finnish Meteorological Institute (Praplan et al., 2017) in order to study seasonal changes of OH reactivity in the boreal forest. Previous studies (Sinha et al., 2010; Nölscher et al., 2012) conducted during summer at the SMEAR II boreal forest site in Hyytiälä, Finland, suggest that a large fraction (50-88%) of the measured total OH reactivity cannot be explained by individual compounds monitored usually in forest air. Development of long-term measurements aims at identifying which periods are more prone to high unaccounted reactivity.

In the present study total OH reactivity measurements were conducted in spring and summer 2016 at the same boreal forest site SMEAR II. Diurnal and seasonal reactivity variations were investigated. Various volatile organic compounds (VOCs) were simultaneous measured by on-line gas chromatography (GC) coupled to a mass spectrometer (MS). On two occasions sampling of additional VOCs and oxidized VOCs followed by off-line analysis by gas and liquid chromatography for up to two weeks enabled further investigation of unknown OH reactivity, derived from the difference between the experimental total OH reactivity and the reactivity calculated from all the individual compounds measured.

METHODS

For the CRM method pyrrole (C₅H₅N) is mixed with zero air and ambient air alternatively. OH is produced by the photolysis of water (H₂O) using ultraviolet (UV) radiation and introduced in the reactor. In the zero air mixture, all OH are consumed by pyrrole (C₂ level), while ambient air contains other reactive compounds that compete for OH leading to a higher pyrrole concentration (C₃ level). The concentration of pyrrole in the absence of OH (C₁ level) is measured by introducing a large concentration of 0.6% propane in N₂ to act as an OH scavenger (Zannoni et al., 2015). C₁ takes into account the photolysis of pyrrole due to the UV radiation entering the reactor, decreasing the pyrrole concentration from the total amount of pyrrole injected in the reactor (C₀ level).

The original CRM instrument (Sinha et al., 2008) used a proton-transfer-reaction mass spectrometer (PTR-MS) to monitor the concentration of pyrrole in the reactor, while the system deployed in the present study uses a gas chromatograph (SYNTECH SPECTRAS Analyser GC955, Synspec BV, Groningen, The Netherlands) with a time resolution of 2-minutes. Every 8 minutes the system switches between measurement of zero air and ambient air. The total OH reactivity \( R_{eq} \) is then derived from the following equation:
with $k_p$ the reaction rate coefficient of the reaction between pyrrole and OH ($1.2 \cdot 10^{-10}$ cm$^3$ s$^{-1}$, REF). $C_3$ should be corrected for the difference in relative humidity (RH) with $C_2$ to take into account the variation of OH concentration due to the change of humidity.

Ozone ($O_3$) has been found to increase the amount of OH in the reactor, due to its photolysis and subsequent reaction with water, which needs to be taken into account by correcting $C_3$ (Praplan et al., 2017). Additional correction factors due to the presence of nitrogen oxides ($NO_x$) need to be applied as well (Dolgorouky et al., 2012; Michoud et al., 2015). Nitrogen oxide (NO) reacts with the peroxy radical ($HO_2$) to produce additional OH, while nitrogen dioxide ($NO_2$) is converted to NO in the CRM system (by photolysis and possibly surface reactions), also leading to an increase in OH levels. However, due to the low NO$_x$ concentrations at the measurement site, this correction remains negligible.

The dilution factor $D$ due to the mixing of sampled air with the nitrogen flow carrying H2O through the UV lamp to produce OH is used to derive the experimental total OH reactivity, $R_{exp}$:

$$R_{exp} = R_{eqn}D$$

Equation (1) assume first-order kinetics ($[C_4H_5N] >> [OH]$), however the $C_4H_5N/OH$ ratio varies between 0.99 and 5.35. A model-based or an empirical correction factor $F$ needs to be applied, but the results presented here do not include yet this correction factor as no gas standard representing the varying composition of the forest air is available and the air composition is not sufficiently well characterised to use a model approach. Therefore, the results are considered preliminary.

In addition to total OH reactivity measurements reactive organic compounds were also measured with two in situ GC-MS (for C$_6$-C$_{10}$ hydrocarbons and oxygenated compounds). Additional sampling took place on two occasions in canisters and through adsorption cartridges (24h time resolution) to be analysed by GC-FID (C$_2$-C$_6$ hydrocarbons) and LC-UV (carbonyls), respectively. The reactivity $R_{OH}$ derived from the sum of individual compounds $X_i$ combined to their respective reaction rate coefficient with OH ($k_{OH+X_i}$) is calculated according to the following equation.

$$R_{OH} = \sum_i k_{OH+X_i} [X_i]$$

Our analysis includes over 100 individual species from two GC-MS, GC-FID and LC-UV measurements. In addition nitrogen oxides, ozone, sulfur dioxide, and carbon monoxide were retrieved from the mast of the SMEAR II station, about 80 m away from the sampling position of total OH reactivity and VOCs.

RESULTS AND DISCUSSION

The preliminary experimental total OH reactivity values measured ($R_{exp}$) are displayed in Figure 1. The average reactivity measured between 15 April and 30 July is $12.4 \pm 8.9$ s$^{-1}$. This average is slightly higher than previous studies in summer at the same site (Sinha et al., 2010; Nölscher et al., 2012). Higher reactivity values were usually found at night, following the BVOCs concentrations pattern, except for high afternoon values observed during the week after soil temperature rises the first time above 1.5°C that year. Previous studies conducted in summer did not capture such high values as observed during this episode in spring 2016.
CONCLUSIONS

Overall the total OH reactivity $R_{OH}$ derived from measurements of over 100 individual compounds is much lower than the experimental total OH reactivity $R_{exp}$ measured at the boreal forest station SMEARII during a period covering over two months of measurements. Diurnal patterns with higher values at night are observed for both $R_{OH}$ and $R_{exp}$. Therefore, the reactivity in the boreal forest is not solely driven by biogenic emissions from vegetation. During spring 2016, high reactivity values were identified in the days following the thawing of the soil at the station. The emitted compounds or their reaction products might be different type of VOCs that were not monitored and are difficult to sample and analyse in situ and off-line due to their high reactivities.

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REFERENCES


EDDY COVARIANCE INSTRUMENT COMPARISON (ONGOING)

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Keywords: eddy covariance, CO\textsubscript{2} flux, spectroscopic corrections.

INTRODUCTION

The eddy covariance (EC) technique is at the moment the most advanced technique for flux assessment. It allows the direct and continuous measurement of fluxes at the ecosystem scale, without interfering with the studied phenomena. The technique is based on the simultaneous high-frequency (> 10 Hz) measurement of the turbulent vertical wind velocity fluctuations and the turbulent gas concentration fluctuations; the covariance of the fluctuations is proportional to the gas flux (Aubinet et al., 2012). The post-processing of the data is, however, very demanding. Many corrections have to be applied, and their effect on the final fluxes has a large magnitude (it can be up to 50% of the flux). Some of the corrections are inherent to the technique, because their need arises from the nature of turbulence itself and the inability of any instrument to fully resolve all the time scales of turbulence. Conversely, some other corrections could in theory be avoided. One of these comes from the fact that the wind speed and the gas concentrations are usually measured in two different volumes: typically two instruments are used, a sonic anemometer and a gas analyser, and they cannot operate in the same volume. This problem is called “sensor separation”. Recently, Campbell Scientific developed an instrument for EC measurements called Irgason, which is the first instrument to integrate the sonic anemometer and the gas analyser. With the Irgason, the wind velocity and the gas concentrations are measured in the same volume, and the sensor separation problem is overcome. The first studies made using the Irgason, however, yielded some unrealistic results (CO\textsubscript{2} uptake during the night over lakes or vegetation), which could indicate some issue in the current Irgason software. Recent research has shown that the issue may be related to the gas analyser spectroscopic corrections, which are performed using a slow-response temperature, instead of the fast-response one. In fact, a consistent bias of the CO\textsubscript{2} flux correlated to the sensible heat flux has been found, and a correction has been put forward (Bogoev et al., 2014). In this study, we cooperate with the University of Évora, Portugal, and run a comparison of the fluxes measured by the Irgason (with the recently suggested correction) and by a standard EC setup.

METHODS

For this eddy covariance instrument comparison, the instrument used are:

- EC setup 1:
  Irgason, Campbell Scientific, Inc. (includes sonic anemometer, CO\textsubscript{2} and H\textsubscript{2}O open-path gas analyser, air temperature and RH sensor);

- EC setup 2:
  sonic anemometer µSonic-3 Scientific, Metek GmbH, Germany; enclosed-path gas analyser LI-7200, LI-COR Inc., Nebraska, USA; meteorological station AWS310, Vaisala Oyj, Vantaa, Finland;

- auxiliary measurements:
  4-way net radiometer CNR-1, Kipp & Zonen B.V., Deft, Netherland; water temperature sensors Pt-100; water CO\textsubscript{2} sensors CARBOCAP GMP343, Vaisala Oyj, Vantaa, Finland;
• logging:
  Windows computer.

The instruments are visible in Figure 1.

![Figure 1: the instrument setup.](image)

The study site is lake Vanajavesi, close to the city of Hämeenlinna, in Finland. The instruments are mounted on a wooden raft at the end of a long and narrow peninsula jutting into the lake in Hattula, Häme; the WGS84 coordinates are 61.13431, 24.25864.

CONCLUSIONS

A more comprehensive evaluation of the results is still ongoing. However, the most important finding is that there is a disagreement between the two recorded CO$_2$ fluxes ($F_{CO2}$), which is still dependent on the sensible heat flux (Figure 2).
Figure 2: difference of the two recorded CO\textsubscript{2} fluxes ($\Delta F_{\text{CO}_2}$) as a function of the sensible heat flux (H).

It does not appear that there is a dependency of $\Delta F_{\text{CO}_2}$ on any of the other relevant variables (latent heat flux, wind speed, friction velocity and wind direction). Further work is being carried out on evaluating Irgason performance, with attention to the flux quality parameters, and on devising a proper correction for the Irgason CO\textsubscript{2} flux.

ACKNOWLEDGEMENTS

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SECONDARY ORGANIC AEROSOL FORMATION FROM α-PINENE VERSUS REAL PLANT EMISSIONS: CHEMICAL AND PHYSICAL PROPERTIES

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Keywords: SOA, α-PINENE, BVOC, HYGROSCOPICITY.

INTRODUCTION

Atmospheric aerosols (particles and the surrounding gas medium) in general have effect on human health and on climate (Nel, 2005; IPCC, 2013). They can scatter and absorb solar radiation, and act as cloud condensation nuclei (CCN), and regulate cloud properties (Rosenfeld et al., 2008; Clement et al., 2009). Aerosol particles are also counted as pollution deteriorating air quality (Nel, 2005). A large fraction (up to 90%) of atmospheric sub-micrometre particle mass consists of organic compounds (Jimenez et al., 2009).

Due to the complexity of the biogenic volatile organic compound (BVOC) mixtures emitted by trees and other plants, α-pinene has often been used for simplicity as a reference compound for boreal forest emitted BVOCs. The aim of this study was to look at some of the physical and chemical properties of secondary organic aerosol (SOA) formed from α-pinene, and compare them to SOA formed from a BVOC mix taken from real plants, specifically Scots pines. Main focus was on the chemical composition of the particles, and their hygroscopicity.

METHODS

All the experiments were conducted at the labs of University of Eastern Finland. The experiment campaign consisted of two main parts: BVOC collection, and chamber studies. The first phase was conducted by selecting five healthy pines (Pinus sylvestris), and bringing them into the lab, where each pine was placed in a separate Teflon bag (dimensions 24” by 39”), which was then sealed around the trunk to stop BVOCs from leaking out. Airflow was introduced to each bag simultaneously, filling them with purified air. Two separate methods of collection were used: continuous and short-term. In short-term method, the bags were filled and then left sealed for 3-5 hours, and then all the air from the bags was filtered through the Tenax tubes. In the continuous method, air was circulating constantly into and out of the bags and through the Tenax tubes, up to several days in total. To analyse the actual sampled BVOC mix, three Tenax tubes were analysed with a gas chromatography mass spectrometer (GC-MS) immediately after collection.

The main part of the experiments was conducted in a 10 m³ Teflon chamber, which was operated as a batch reactor (Figure 1). The chamber was filled with humidified air (45% relative humidity at 22 °C). In the cases of photochemical experiments, H₂O₂ was added as OH precursor, and butanol-D9 was added as a tracer for OH. After target conditions were reached in the chamber, selected VOC (α-pinene or real plant BVOC mix) was added, and ozone injected to begin the reactions. In photochemical experiments UV-lights were turned on to signal the start of the experiments. Experiments lasted on average six hours.
Figure 1. Schematic presentation of the experiment chamber set-up. The chamber was operated in a batch reactor mode. Two inlets were used, one for the main humidified flow, and another for VOCs, ozone, and seed. For sampling, there were two separate sample lines out of the chamber, one for particles and another for gas phase.

Five experiments were conducted in total, four with α-pinene as a precursor, and one real plant reference (see Table 1). With α-pinene both ozonolysis and low NO\textsubscript{X} photochemical conditions were probed, while the real plant experiment was in ozone regime only.

<table>
<thead>
<tr>
<th>VOC Source</th>
<th>Oxidation scheme</th>
<th>Seed</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene</td>
<td>O\textsubscript{3}</td>
<td>polydisperse</td>
</tr>
<tr>
<td>α-pinene</td>
<td>O\textsubscript{3} + OH</td>
<td>polydisperse</td>
</tr>
<tr>
<td>α-pinene</td>
<td>O\textsubscript{3} + OH</td>
<td>polydisperse</td>
</tr>
<tr>
<td>pine BVOC</td>
<td>O\textsubscript{3}</td>
<td>polydisperse</td>
</tr>
</tbody>
</table>

Table 1. Overview of conducted experiments. In α-pinene cases, both oxidation scheme experiments were conducted twice. Due to scarcity of BVOC samples, only one real plant emission experiment was conducted, with ozone.

The two main instruments used in this study were the Filter Inlet for Gas and Aerosols, (FIGAERO-CIMS, Aerodyne Research Inc., USA and Tofwerk AG, Thun, Switzerland, see Lopez-Hilfiker et al., 2014) for analysing the chemical composition of the particles, and hygroscopic tandem differential mobility analyser (HTDMA, custom made, described in Väisänen et al., 2016) to measure the hygroscopicity of the particles.

Supporting instruments included a high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-MS, Ionicon) to measure VOC concentrations during chamber experiment, aerosol mass spectrometer (AMS, Aerodyne Research Inc., USA) to get information on particle composition and organic fraction, scanning mobility particle sizer (SMPS, TSI Incorporated, USA) for particle size distribution and number concentration, and ozone monitor (TE49i, Thermo Fischer Scientific).
α-pinene was seen to be the major monoterpene compound emitted by the pines, and sampled into the Tenax tubes. Other major VOC observed were 3-carene, and in smaller concentrations limonene and camphene.

Experiment campaign was finished shortly before submission of the abstract and as such, it is early yet to present any conclusions from the study.

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REFERENCES


LONG TERM EFFECTS OF FIRE ON CARBON AND NITROGEN POOLS AND FLUXES IN THE ARCTIC PERMAFROST AND SUBARCTIC FORESTS (ARCTICFIRE)

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Keywords: FOREST FIRE, GHG EXCHANGE, PERMAFROST, DISTURBANCES

INTRODUCTION

Boreal forests, which are to a large extent located on permafrost soils, are a crucial part of the climate system because of their large soil carbon (C) pool. Even small change in this pool may change the terrestrial C sink in the arctic into a source with consequent increase in CO₂ concentrations. About 1% of boreal forests are exposed to fire annually, which affects the soil and permafrost under them. Thawing of permafrost increases the depth of the active layer containing large C and N stocks. In addition to temperature, the decomposition of soil organic matter depends on its chemical composition which may also be affected by fires. Part of the soil organic matter is turned into pyrogenic C and N resistant to decomposition.

AIMS

The aim of this project is to study the long term effects of fire on the decomposition of soil organic matter (SOM) in the northern arctic and subarctic forests. We are studying the changes in size and quality of soil C and N pools and fluxes after forest fires and their underlying processes in the arctic and subarctic zone, especially the interactions of permafrost and post fire C balances.

METHODS

We studied the effect of forest fires on soil greenhouse gas fluxes (CO₂, CH₄ and N₂O) using portable chambers. The amount of easily decomposable and recalcitrant fractions in soil organic matter were determined with water, ethanol and acid extraction, and the natural ¹³C and ¹⁵N abundances as well as chemical quality with Fourier Transform Infrared Spectroscopy (FTIR) were studied. Also, changes in
microbial community structure and composition were analyzed with next generation pyrosequencing. Finally, in 2016 and 2017, we have studied the effects of wildfires on Biogenic Volatile Organic Compound (BVOC) and nitric acid (HONO) emissions from soils in Värriö and in Central Siberia using portable chambers, Tenax tubes, GC-MS and LOPAP®-03 (Long Path Absorption Photo Meter).

RESULTS

Our results indicate that soil CO$_2$ effluxes were significantly decreased immediately after the fire, and the recovery to pre-fire level took several decades. Soils were a small sink of CH$_4$ and a source of N$_2$O in all age classes, and the CH$_4$ uptake was increased and N$_2$O fluxes decreased still 20 years following the fire. A clear vertical distribution was observed in the amount of extractable soil organic matter the amount of extractable organic matter being highest in the soil surface layers and decreasing with depth. The natural $^{13}$C and $^{15}$N abundances and FTIR spectra and changes in microbial community composition are still under analysis. The preliminary results also suggest that there were substantial differences in BVOC emissions between recently burnt forests and old forest stands and the differences were related to forest floor vegetation (Zhang-Turpeinen et al. unpublished results).

OUR RECENT RESEARCH HIGHLIGHTS ARE AS FOLLOWS:

• In our recent study by Pumpanen et al. (2017) we studied the effects of tree roots and addition of glucose on the solubility of soil organic matter (SOM). Our study showed that SOM can be separated to pools with distinctive isotopic concentrations with pressurized hot water. Roots may induce organic matter degradation and N uptake from soluble SOM fractions. Larger $^{14}$C abundance in soluble SOM indicated it contained older C than the recently assimilated C.

• In our recent paper by Köster et al. (2017), we studied the effect of wildfires on permafrost thawing and greenhouse gas fluxes. We showed that increase in the active layer thickness results in higher GHG emissions. A fire chronosequence study reveals long-term changes in GHG emissions. The only factor affecting studied GHG fluxes is the time since last forest fire. Fire causes long-lasting changes of GHG emissions.

• In our recent paper by Palviainen et al. (2017), we studied the effect of wildfires on nitrogen balance in sub-arctic Scots pine forests in Värriö. Our results show that the non-stand-replacing, intermediate severity fires decrease considerably N pools in biomass but changes in soil and total ecosystem N pools are slight. Current fire-return interval does not seem to pose a great threat to ecosystem productivity and N status in these sub-arctic forests.

• In our recent paper by Sun et al. (2016), we characterized the soil bacterial communities across three different times post fire in a 2 to 152-year fire chronosequence in Värriö by Illumina MiSeq sequencing, coupled with a functional gene array (GeoChip). The results showed that the bacterial diversity did not differ between the recently and older burned areas, suggesting a concomitant recovery in the bacterial diversity after fire. Soil temperature, pH and water contents were the most important factors in shaping the bacterial community structures and function. This study provides functional insight on the impact of fire disturbance on soil bacterial community.

Recent publications of the group on the disturbance effects on forest carbon and nitrogen cycles:


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MEASURING THE TEMPERATURE RESPONSE OF α-PINENE-DERIVED HIGHLY OXYGENATED MOLECULES (HOMs) IN A COLD-ROOM SMOG CHAMBER

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Keywords: HOMs, CI-API-TOF, Cold-Room SMOG Chamber, Temperature.

INTRODUCTION

The vegetation is known to emit various volatiles from which, after atmospheric oxidation processes, Highly Oxygenated Molecules (HOMs) can be formed (Ehn et al., 2012). These HOMs were shown to play a key role in the formation of Secondary Organic Aerosols (SOA) and the growth of the smallest particles (Ehn et al., 2014; Tröstl et al., 2016). In this work, we discuss the results of HOM measurements performed in the Aarhus University Research on Aerosol (AURA) smog chamber (Kristensen et al., 2017) during Ozonolysis experiment at different temperatures. By simulating the atmospheric oxidation processes between α-pinene and ozone, we aim at better characterising the role that temperature has on the chemistry involved in the formation and the evolution of the HOMs.

METHODS

The experiments took place in the 5 m³ AURA chamber (Kristensen et al., 2017) set at a fixed temperature (20 °C, 0 °C, or -15 °C). Operated in batch mode, the α-pinene (10 or 50 ppb) was injected with 100 ppb of ozone dispersed in filtered air, initially present in the chamber. The resulting highly oxidized products of α-pinene ozonolysis were measured with a high-resolution nitrate-based Chemical Ionization (CI) Atmospheric Pressure interface Time-Of-Flight (API-TOF) mass spectrometer (Tofwerk AG, Thun, Switzerland & Aerodyne Research Inc., USA), described previously by Jokinen et al. (2012).

When clustered to Nitrate (NO₃⁻) during chemical ionisation, α-pinene-derived HOM-monomers are typically seen in the mass range 300-400 Th and present a chemical composition of C₁₀H₁₄O₇. Figure 1 shows HOM-monomer mass spectra, in the aforementioned range, at 20 °C, 0 °C and -15 °C, respectively, averaged over a 10 minutes sampling time after the injection of α-pinene (a), and 30 min after the VOC injection (b), both at high concentration of the volatile precursor (i.e. 50 ppb). From this example, a significant decrease of the signal, thus of the concentration, can be seen the cooler the reaction temperature is, for both cases. Additionally, a variation in the distribution of the most abundant species can be depicted between the different temperatures at which the spectra were recorded revealing an extensive change of chemistry involved in HOMs formation.
Figure 1. Mass spectra of high-mass compounds present in the gas phase during high-VOC load experiments, at 20 °C (orange), 0 °C (green) and -15 °C (blue). Most abundant species, in C_{10} typical carbon skeleton, were tagged and identified from first analysis of high resolution data. The presented data were acquired, and averaged over 10 min, from a few minutes following the VOC injection (a) and 30 min after the start of the experiment (b).

We performed further analysis targeted on specific chemical compounds, or group of molecules, in order to characterize their evolution as a function of the advancement of the experiment (i.e. time after the VOC injection, thus α-pinene remaining). As an example, total monomers (i.e. any compound with a chemical formula within C_{10}H_{14}O_{7-11}), and individual compounds C_{10}H_{14}O_{7}, C_{10}H_{14}O_{9} or C_{10}H_{14}O_{11} were traced for the different temperatures and are presented in Figure 2. Herein, the key steps of an experiment can be identified (i.e. background, injection and stabilization of the HOMs produced) and furthermore characterize the formation rate for the selected chemical entities.

Figure 2. High resolution time traces for selected compounds formed in high α-pinene concentrations. The panel (a) represent the sum of HOM monomers having a typical chemical composition C_{10}H_{14}O_{7-11}. In (b) are shown specific HOMs characterized by a chemical composition in C_{10}H_{14} containing 7 (full line), 9 (dashed line) or 11(dotted line) oxygen atoms. The measured ions are shown as clusters with nitrates due to chemical ionization. Temperatures are depicted as following: orange for 20 °C, green for 0 °C, and blue for -15 °C.
CONCLUSIONS

This on-going study investigates the variability of HOM formation at different temperatures, comparing the differences in both the chemical composition and the abundance. Colder temperatures significantly decreased the HOM production. Interestingly, some HOMs were not seen to decrease at the same rate as a function of the temperature, suggesting a shift from semi to low volatility of these species at colder temperature. A manuscript is being prepared about the work outlined here, with emphasis on the formation and physical properties of these highly oxidized molecules with temperature.

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REFERENCES

HIMMELI – Helsinki Model of Methane build-up and emission for peatlands

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INTRODUCTION

Peatlands emit methane (CH₄) because their water-saturated soils are anoxic and the anoxic decomposition of soil organic matter is partly carried out by methanogenic CH₄-producing microbes (Nilsson and Öquist, 2009). A fraction of the produced CH₄ can be oxidized to CO₂ by methanotrophic bacteria before emission to the atmosphere. CH₄ production, oxidation and different transport routes in peat have been described in several peatland models (Xu et al., 2016).

HIMMELI, Helsinki Model of Methane build-up and emission, simulates the CH₄ processes in a layered peat column. It is not a full peatland carbon cycle model but it needs the rate of anoxic soil respiration as input and calculates the CH₄ emissions driven with soil temperature, water table depth (WTD) and leaf area index (LAI) of gas-transporting peatland vegetation. Oxygen (O₂) and CO₂ transport and concentrations are also simulated and the O₂ concentrations affect both the CH₄ production and oxidation rates. The process descriptions in HIMMELI were largely adopted from earlier CH₄ models (e.g. Arah and Stephen, 1998; Wania et al., 2010) and the aim was to develop a flexible module that can be easily combined with different peatland models to simulate CH₄ emissions. In order to prepare for this, we conducted several tests on HIMMELI (Raivonen et al., 2017). Here we summarize the findings.

METHODS

We tested HIMMELI by analyzing its sensitivity 1) to the driving data (anoxic respiration, soil temperature, LAI and WTD) and 2) to the peat column depth and peat layer thickness. The former was
analyzed using steady-state tests and the latter by running HIMMELI with measured input data from the Siikaneva peatland site (Rinne et al., 2007) using different peat column descriptions. In addition, we compared the output CH$_4$ fluxes to fluxes observed at Siikaneva, in order to verify that HIMMELI is capable of producing realistic CH$_4$ fluxes when the input is within realistic limits. Model parameters used in the study were mainly taken from literature but a set was obtained by optimizing the model for Siikaneva using Bayesian methods (Susiluoto et al., 2017).

RESULTS AND DISCUSSION

The sensitivity tests indicated that the simulated CH$_4$ emissions depend strongly on the CH$_4$ production rate and CH$_4$ oxidation plays a smaller role. As CH$_4$ production was inhibited by O$_2$ in the model, factors that affected the O$_2$ transport rates and O$_2$ concentrations in the peat also controlled the CH$_4$ production and emission rates, when input anoxic respiration was constant. For example, as in these mechanistic sensitivity tests the anoxic respiration rate was not dependent on LAI but LAI only affected the gas transport capacity of the vegetation, increasing LAI decreased the CH$_4$ emissions because of increasing O$_2$ transport and inhibition of CH$_4$ production. As a general conclusion, when the anoxic respiration input for HIMMELI is constant, the output CH$_4$ emission level depends on how much O$_2$ is available in the inundated peat layers that produce the CH$_4$.

We found that the description of the peat column did not have any significant impact on the simulated CH$_4$ fluxes. When the input (including the anoxic respiration rate) was constant, varying the peat column depth and/or layer thickness affected the output only slightly. The reason for this probably is the way HIMMELI handles the anoxic respiration input. CH$_4$ production is assumed to be connected to living plant roots. Thus, the anoxic respiration and CH$_4$ production is vertically distributed along a root distribution function (Wania et al., 2010) that determines most of the root mass in the topmost peat layers. CH$_4$ production allocated in the bottom is minor.

We modelled the anoxic respiration for the Siikaneva peatland site using estimated net primary productivity (NPP) and a model of peat respiration (Schuldt et al., 2013) as the basis. Running HIMMELI with it and observed WTD, observed peat temperature profile and simulated LAI, resulted in CH$_4$ emissions that were comparable to the observed CH$_4$ emissions. This model thus seems to be able to output realistic CH$_4$ emissions with different set-ups and can in future be tested in combination with peatland models that provide the required input.

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A NEW OPTICAL CHAMBER METHOD TO QUANTIFY THE SEASONAL VARIATION IN AMBIENT AND 77K LEAF-LEVEL CHLOROPHYLL FLUORESCENCE SPECTRA

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Keywords: BOREAL FOREST, PHOTOSYNTHESIS, SOLAR-INDUCED FLUORESCENCE, SPRING RECOVERY

INTRODUCTION

Chlorophyll fluorescence (ChF) has been widely used as a tool for tracking changes in photosynthetic activity for decades (Pedrós, 2008). ChF can, for example, reflect the variation in photosynthesis in stress conditions (Agati et al., 1995). However, a number of questions still remain open, as to how the shape and intensity of the fluorescence spectra is connected to the mechanistic acclimation of photosynthesis. This is particularly critical at the leaf-level, which is the smallest scale at which spectral fluorescence can be measured in vivo, and especially for conifer needles which are difficult to measure due to their complex geometry.

The interpretation of the ChlF signal acquired at room/physiological temperatures is in part complicated by the spectral overlap in fluorescence properties of photosystem II and I. In contrast, at liquid nitrogen temperature (77K) the fluorescence spectra from each photosystem can be separated where the red fluorescence peak corresponds to PSII and the far-red peak to PSI (Baker, 2008). It would therefore be highly informative to measure both ambient and 77K fluorescence spectra from the same sample.

One of the goal of our recent campaign (“Fluorescence Across Space and Time”- FAST, February 9th – July 11th 2017, Hyytiälä Forest Station, SMEAR II, Finland), was to develop a new optical chamber and protocol for measuring ambient and 77K spectral fluorescence in intact leaves. The new protocol was used to quantify the seasonal variation in leaf-level fluorescence properties across boreal species, during the spring recovery of photosynthesis and at different canopy heights. The resulting data can be used to study the mechanisms that control the leaf-level variation in the ChlF signal and its connection with photosynthesis, across species, canopy positions and during the season.

METHODS

We used the new optical chamber to follow the ChlF properties in a total of five species (N=3, biological replicates). Species included: two conifers (Pinus silvestris and Picea abies), a broadleaf tree (Betula pendula) and two ground species (Vaccinium vitis-idaea and Vaccinium myrtillus).

The optical chamber setup was based on a 3-D printed PLA plastic cuvette and a series of detachable metal plates where the samples could be arrange and fixed beforehand. A black tape of known reflectance was used to attach the sample to metal plate. A bifurcated reflectance probe (Ocean Optics®, R600-7-UV-125F) was coupled to a halogen light source (Ocean Optics®, HL-2000) via a filter-carrier (Ocean Optics®, FHS-UV) and fiber bundle (Thorlabs®, BF20HSMA01). It was afterwards connected to VIS-NIR spectrometer (Ocean Optics®, USB2000+) leading the signal to the computer. The short-pass 650nm filter (Thorlabs® FESO650) held in filter-carrier facilitated the measurement of the fluorescence spectra above 650nm. A fiber holder (Ocean Optics®, RPH-1), mounted at the end of reflectance probe, enabled a stable connection between the system and leaf sample.
The crucial advantage of the optical chamber method is an ability to measure reflectance, fluorescence in room temperature and fluorescence in 77K of each sample at the identical footprint. We were therefore able to conduct the corresponding measurement of fluorescence at two different physical states in analogous manner. At ambient temperature the fluorescence spectra gives us information on the acclimation of photosynthesis. This is also the spectra of the solar-induced chlorophyll fluorescence that can be measured from towers, drones or satellites (See Abstract by Porcar-Castell). However, because the fluorescence emissions of PSII and PSI are overlapped the interpretation of ambient temperature fluorescence spectra is not straightforward. At 77K, the two main fluorescence peaks can be distinctly attributed to photosystem I and II populations in the leaf (Govindjee, 1995) giving us supporting information to understand the fluorescence dynamics of each of the photosystems and their impact on ambient fluorescence spectra. That co-supplementation of data would be impossible to achieve if the sample footprint was not identical in two measurements.

PRELIMINARY RESULTS AND FURTHER ANALYSIS

The data collected during the FAST campaign is being currently analyzed. Here we present an example of two conifer species (Fig. 1) considering the seasonal variation on fluorescence signal at different position within the canopy profile in ambient temperature and 77K.
In agreement with literature (Verhoeven, 2013, Springer et al., 2017), all the plots show that there is a distinct dissimilarity in fluorescence signal between species, in both its intensity and spectrum shapes (peak locations). In ambient temperatures, low canopy needles emit significantly higher fluorescence signal than top-canopy individuals, which is even more pronounced in case of pine. In both examples, the lowest fluorescence signal values are represented by spring top canopy samples, while the timing of maximum fluorescence emission is species-specific.

In 77K, low and top canopy needles fluorescence signals reveal similar shapes and the differences in intensities stays quite consistent across seasons. The relation varies, however, while taking into account the wavelength range of fluorescence emission. Both seasonal and vertical changes in far-red can be caused by i) structural changes in PSI (representative wavelength range - 740nm) or ii) by reciprocal changes in the cross-sections of PSI and PSII for light absorption. We expect to reveal the actual cause of observed 77K-ChF spectra shape variability through further analysis.
Moreover, we will analyze the fluorescence spectra for remaining species, in order to determine their specific characteristics. We will examine distinctions between canopy positions and available light conditions in the seasonal perspective. Ambient and 77K results will be used to evaluate the photosystems’ contributions into fluorescence signal. At last, we aim to compare the leaf-level fluorescence data with results of other measurement carried out within the FAST campaign.

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Isoprene and monoterpene emissions from a boreal peatland during spring and early summer

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Keywords: BVOC, flux, wetland, PTR-TOFMS.

INTRODUCTION

Emissions of biogenic volatile organic compounds (BVOC) have a significant impact on the regional boreal climate (e.g. Paasonen et al., 2013). However, the estimates are uncertain, partly due to the limited measurement network (Guenther et al., 2006; Rinne et al., 2016). For example, BVOC measurements on different wetland types have been almost totally excluded, with some exceptions (Holst et al., 2010), even though fens cover 0.3 – 0.5 · 10⁶ km² in the boreal and arctic zones in Eurasia and North America (Rinne et al., 2007). In that sense, BVOC emissions might have a major regional contribution to the BVOC budget. Understanding the dynamics of the BVOC exchange in wetlands is then crucial as Rinnan et al. (2014) and Kramshøj et al. (2016) have speculated with dramatical changes in the BVOC emissions in the arctic zone in future.

Therefore, we organized a measurement campaign in the boreal peatland Siikaneva between March and June 2016 to study BVOC exchange and its effects on both air chemistry and aerosol formation. In this abstract, we present isoprene and monoterpene flux time series from this campaign.

METHODS

The measurements were obtained in an ombrotrophic bog, which is a part of the Siikaneva peatland complex in Southern Finland, located in the southern boreal vegetation zone (61° 50.179’ N, 24° 10.145’ E). Siikaneva has a permanent measurement station (e.g. Rinne et al., 2007; Korrensalo et al., 2017, Fig. 1) that will be also a part of the ICOS-network (Integrated Carbon Observation System).

In this study, the measurements were performed around 50 m north from the permanent station. The PTR-TOFMS (proton transfer reaction time-of-flight mass spectrometer, Ionicon Analytic Gmbh, see Jordan et al., 2009) was located in a measurement cabin with an inlet line sampling from a tripod type of measurement mast. The inlet was located just below the anemometer (Metek USA-1) at the height of 2.7 m. The campaign lasted from March 1 until June 19 2016. During this period, the instrument was calibrated seven times using a diluted standard gas (Apel-Riemer). The background signal was measured three times per day using a custom made catalytic converter. The calibrations and volume mixing ratio calculations were done similarly as described in Schallhart et al. (2016). The fluxes were calculated using the eddy covariance technique (e.g. Aubinet et al., 2012).
RESULTS AND CONCLUSIONS

The measurements were conducted during four months – from March to June – with the ambient temperature varying between −10 and 20 degrees (daily averages, see Fig. 2). During winter, both isoprene and monoterpene fluxes were below the detection limits. Isoprene emissions started to increase from the beginning of May and were almost as high as the monoterpene emissions at the SMEAR II site, pine forest, in June (Fig. 2). Reversely, monoterpene emissions remained low the whole campaign, being still detectable in May and June. The detectable monoterpene flux is an interesting result since typically monoterpenes are excluded from wetland emission studies. Monoterpenes could have also originated from the forest close to the station, however, the footprint analysis showed the forest having only a minor contribution (Fig. 3).

Isoprene flux dynamics followed the traditional pattern (Guenther et al., 1991) with maximum flux around midday and zero flux at nights (Fig. 4). On the other hand, monoterpene fluxes showed more interesting behaviour without any diurnal cycle at all (Fig. 4). In other words, monoterpene emissions seemed to be independent of the short scale temperature variations in Siikaneva.
Monoterpene fluxes correlated significantly with methane fluxes, even though the correlation coefficient was low ($r = 0.39$). However, this indicates that monoterpenes and methane may have the same sources. The diurnal behaviour is also similar for both compounds. This could indicate that monoterpenes are produced deeper in the soil, possibly even in anaerobic conditions by bacteria fauna similarly as methane.

In future research, other detected compounds will be also analysed carefully. We will focus especially on the emission dynamics and the deposition of BVOCs.

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INTRODUCTION

Extra-tropical cyclones are ubiquitous in the mid-latitude atmosphere, occurring most frequently during the winter season. They affect our everyday life by inducing variations and extremes of weather, sometimes even to extent which can cause huge civil impacts to the society (e.g. Wernli et al. 2002; Fink et al. 2009). Mid-latitude cyclones are also important drivers of heat and momentum, and are thus necessary for the atmospheric general circulation.

A large number of previous studies have been done which investigate e.g. the changes in the intensity, frequency, and tracks of extra-tropical cyclones in a warmer climate. All of these changes in cyclone characteristics partly result from the different atmospheric temperature distribution in the future climate. For example, climate change projections made with General Circulation Models (GCM) suggest that at mid-latitudes, the meridional low-level temperature gradient will decrease whereas at upper levels it will increase (e.g. Woollings 2008; Catto et al. 2011). In this study, the sensitivity of extra-tropical cyclones to environmental temperature changes is investigated using idealised simulations.

Thus, in our study, three 10-day long idealised model experiments and a control run are performed. The temperature forcings in the experiments are similar to what are expected in the warmer climate: 1) uniform increase of atmospheric temperature, 2) decreased lower level temperature gradient and 3) increased upper level temperature gradient. To assess the changes in the pure dynamics of the cyclones, the experiments are conducted first without atmospheric moisture. After that, similar experiments are done in a moist environment.

METHODS

This study was conducted with the Weather Research and Forecast (WRF) model v. 3.8.1 (Shamarock et al., 2008), using its idealized mode in a Cartesian geometry and with periodic east-west boundaries. The simulations were run for 10 days, in a domain of 5000 km x 8000 km x 16 km, and with 50 km horizontal grid spacing. The initial conditions of zonal wind and temperature were typical for Northern Hemisphere wintertime.

Three sets of experiments were performed. Firstly, in Experiment Uni, the temperature was increased uniformly everywhere in the model domain by $T_0 = 2, 4$ and 6 K. Secondly, in Experiment Low, the meridional temperature gradient in the lower troposphere was decreased. The decrease was done by simply warming the northern part and cooling the southern part of the domain by $T_0 = 2, 4$ and 6 K. The temperature change in the meridional direction of the domain was linear, with zero change in the middle of the domain. Thirdly, in Experiment Up, the meridional temperature gradient in the upper troposphere was increased. This was done by modifying the meridional temperature gradient in the same way as in Experiment Low but to the opposite direction. In the vertical direction, the gradient changes in both experiments were slowly attenuated to the level of 600 hPa. Finally, the control run with no temperature changes was performed.
As already mentioned, we conducted first the experiments in a dry mode. The absence of moisture in the dry experiments simplifies the dynamics of the simulated weather system, and in that way helps to discover the consequences of the environmental temperature changes without the effect of latent heat release. In our dry experiments the atmosphere was kept dry throughout the whole simulation. Finally, similar experiments were performed with full physics and moisture.

Figure 1: Surface pressure (contours) and 850 hPa temperature (colors) in a) dry and b) moist control runs at the time of half eddy kinetic energy maximum.

**RESULTS**

Figure 1 gives a brief look to the structure of the cyclone in the dry and moist control runs, at the time when their eddy kinetic energy has reached half of its maximum. The cyclone without moisture (Fig. 1a) is less deep and has weaker pressure gradient around the center compared to the one with moisture (Fig. 1b). This is because diabatic heating, dominated by latent heat release, acts as a deepening mechanism in this idealized baroclinic wave simulation (Rantanen et al. 2017). However, in both simulations the initial disturbance develops eventually to a very typical, text-book type extra-tropical cyclone.

Figure 2 shows the time evolution of minimum surface pressure and eddy kinetic energy for both dry and moist simulations, and for all of the experiments (only $T_0 = 6$ runs shown). Firstly, besides being deeper (compare Fig. 2a and 2b), the cyclones formed in a moist atmosphere have also clearly more kinetic energy (compare Fig. 2c and 2d) than the ones formed in a dry environment. Furthermore, the response to temperature forcings is seemingly greater in the moist simulations. This emphasizes the effect of moisture in the atmosphere: the results in Fig. 2a and 2c can be understood as changes in the adiabatic dynamics of the cyclone, which are to some extent masked by the effect of moisture in Fig. 2b and 2d.

For the dry Experiment Uni, the cyclone formed in a 6 K warmer environment ends up slightly weaker than the control run (Fig. 2a and Fig. 2c, red line). This modest weakening of the
Figure 2: Time evolution of a) the minimum surface pressure in dry experiments, b) the minimum surface pressure in moist experiments, c) eddy kinetic energy in dry experiments and d) eddy kinetic energy in moist experiments. For simplicity, in addition to the control run, only the $T_0 = 6$ runs from each experiment are expressed.

cyclone with the warming in the dry simulations is related to the weakening of the jet stream due to the warming. However, diabatic processes become important when the moisture enters to the simulations. Warming of the whole domain by 6 K raises naturally the atmospheric moisture content, which then materializes as an increased latent heat release in the vicinity of the surface low. This enhanced diabatic heating makes the surface low deepen vigorously in the Uni moist experiment (Fig. 2b, red line). However, this cyclone has lowest maximum eddy kinetic energy of all experiments, including the control run (Fig. 2d). This is because increased latent heat release in the mid-troposphere raises geopotential heights in the upper troposphere, which then leads to weakened wind field and decreased kinetic energy.

The time series of minimum surface pressure and eddy kinetic energy of Experiment Low also presented with yellow lines in Fig. 2. In this experiment, the low level meridional temperature gradient was decreased. The results were somewhat as expected: the cyclone formed within the area of reduced temperature gradient remains weaker, regardless of whether moisture is present or not. This is reasonable since the baroclinicity acts as a source for the growth of the baroclinic waves: when it is decreased, the cyclones do not have as much energy to be utilized for their evolution.

Lastly, as the Fig. 2c reveals, the increase of baroclinicity in the upper troposphere does not increase the kinetic energy of the cyclone in the dry simulations. This was because increased wind speed at upper levels leads to a faster propagation of the upper disturbance, which further emerges
as unfavored phasing of the temperature and wind fields. However, this feature is not visible in moist runs: both the minimum surface pressure (Fig. 2b, violet line) and eddy kinetic energy (Fig. 2d) indicate that the intensity of the cyclone is increased with the increased temperature gradient in the upper troposphere.

CONCLUSIONS

The response of extra-tropical cyclone dynamics to different types of environmental temperature changes is investigated by using idealised baroclinic wave simulations of the WRF model. The temperature forcings in 10-day long model experiments are similar to what are expected in a warmer climate: 1) uniform temperature increase, 2) decreased lower level temperature gradient and 3) increased upper level temperature gradient. In order to separate the influence of moisture from the changes in the cyclone dynamics, all three experiments are performed both in a dry and a moist atmosphere.

The results suggest that the dynamics of extra-tropical cyclones are most sensitive to the changes in the lower tropospheric temperature gradient. When the gradient is decreased, the resulting cyclone is weaker and has less kinetic energy. This holds true in both dry and moist atmosphere. However, the same does not apply for the upper troposphere. Increased upper level temperature gradient accelerates jet streams significantly at the same levels, leading to unfavored phasing between temperature and wind fields. This mechanism decreases the kinetic energy of the cyclone in the dry atmosphere, but this feature is masked behind the effect of moisture in the moist simulations. The results show also that the uniform increase of temperature can induce deep cyclones driven by diabatic processes, but their dynamic properties (like kinetic energy) can be very modest.

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REFERENCES


TRANSPERSION REGULATES THE EMISSIONS OF WATER-SOLUBLE SHORT-CHAINED OXEOCS IN SCOTS PINE (PINUS SYLVESTRIS)

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Keywords: OXOC, methanol, acetone, acetaldehyde, Scots pine, xylem flow, transpiration

INTRODUCTION

The models describing plant emitted volatile organic compounds (VOCs) are mainly based on temperature and / or light, and typically contain no other physiological controls. However, as short-chained oxygenated volatile organic compounds (OXOCs), such as methanol, acetone and acetaldehyde, are soluble to water (Henry’s law coefficient under 100 Pa m³ mol⁻¹), stomatal control can regulate their emissions from leaves as shown by Niinemets 2003 and Harley et al. 2007. Even stronger relations have been found between these compounds’ emissions and transpiration (Folkes et al. 2007, Filella et al. 2007 and 2009, Harley et al. 2007), which indicates that also transport in xylem water affects the emission patterns. In addition, Hölttä and Kolari (2009) and many other studies have shown that even CO₂, with lower partitioning to aqueous phase, is transported in xylem water. We studied the roles and interactions of temperature, stomatal conductance and transpiration in explaining methanol, acetone and acetaldehyde emissions from Scots pine using long term field measurements.

METHODS

Shoot scale fluxes of CO₂, water vapour and VOCs are continuously measured at SMEAR II site in Hyytiälä by a dynamic chamber system explained in detail by Kolari et al. (2012) since year 2009. We used data of methanol, acetone and acetaldehyde fluxes, temperature, and transpiration calculated from water vapour flux from years 2010, 2011, 2013 and 2014. Years 2010, 2011 and 2013, the measurements were from 1-year-old shoot without actively growing buds. In year 2014, the measurements were from growing bud. In addition, stomatal conductance was calculated as the ratio between evapotranspiration rate and vapour pressure deficit. We studied the roles of temperature, stomatal conductance and transpiration on methanol, acetone and acetaldehyde emissions individually and together by regression analysis. To examine also the interactions and relative importance of these variables, we used path analysis tools by R code lavaan (Rosseel 2012). In first path model, we included only the effects of temperature and stomatal conductance as suggested by Niinemets et al. (2003). In the second path model, we added transpiration.

RESULTS

We found that temperature was the single variable best explaining methanol emissions (R² 0.51 on average), but transpiration in explaining acetone (R² 0.54 on average) and acetaldehyde (R² 0.56 on average) emissions from pines. Stomatal conductance alone explained the emissions very poorly. For all the compounds, the best regressions model combining the exponential effect of temperature and linear effect of transpiration (R² 0.67, 0.61 and 0.62 on average, for methanol, acetaldehyde and acetone respectively) (Figure 1). The path models further indicated, that a part of temperature’s effect and all of stomatal conductance’s effect on emissions are mediated through transpiration.
Estimate T: \( b1 \times \exp(0.09 \times (T - 303)) \)
Estimate E: \( b2 \times E \)
Estimate C: \( b3 \times \exp(b4 \times C) \)
Estimate T+E: \( b5 \times \exp(\beta \times (T - 303)) + b6 \times E \)
Estimate T+G: \( b7 \times \exp(\beta \times (T - 303)) + b8 \times \exp(b9 \times C) \)

CONCLUSIONS

In a similar way as in CO2 emissions dynamics, transport in xylem water has a role in emission dynamics of methanol, acetone and acetaldehyde. Stomatal conductance affects the emissions mainly by controlling transpiration and some of temperature’s effect is also related to transpiration.

REFERENCES


Climate change expertise is urgently needed in all fields of the society. In Finland, however, there has been severe shortcomings in teaching the basics of climate change in many universities and study fields, although, at least to some extent, climate change has been included in teaching in all universities (Liljeström and Monni, 2015).

NEW ONLINE LEARNING MATERIAL

Climate.now is a multidisciplinary learning material about basics of climate change published online in Autumn 2016 at www.climatenow.fi. It is aimed at higher education and is available online for anyone to use.

The Climate.now material is located at the University of Helsinki MOOC platform (www.mooc.helsinki.fi). Material consists of text, figures, video and assignments. It covers the topic of climate change from different perspectives: from physical background to ecological and societal effects as well as adaptation. One important goal of the course is to reinforce the student’s understanding of climate change as a human and societal challenge and to give everyone the means to participate in resolving it. All material is available both in English as well as in Finnish.

The Climate.now material includes a detailed plan for a climate change course that can easily be applied by a university teacher when starting a new course. By answering to multiple choice questions, student gets an automatic certificate. To get credit points, student needs to register to one of the university courses organized based on the material.

MULTIDISCIPLINARY COLLABORATION

Climate.now was made in collaboration with multidisciplinary experts from University of Helsinki, Lappeenranta University of Technology, Metropolia University of Applied Sciences and Finnish Innovation Fund Sitra. Experts of natural sciences, technology, pedagogy as well as arts were included.

The Climate.now learning material can be freely used by any universities or other institutions, like companies, as a study material for a climate change course. Currently there are courses going on at the University of Helsinki, Lappeenranta University of Technology, Aalto University as well as University of Jyväskylä in Finland. Courses have attracted students from different disciplines - from natural sciences and technology to business and social sciences.
Experiences from the first courses have been inspiring. Students have found multidisciplinary courses challenging. On the other hand, multidisciplinary applied projects were found as best learning methods during the courses. Climate change was found both as a motivating and depressing topic to study.

In Autumn 2017 the Climate.now material was transferred from Sitra to University of Helsinki. University of Helsinki coordinates the collaboration between universities as well as updating of the material that is to be continued at least until 2019, with the funding from the Finnish Innovation Fund Sitra.

CONCLUSIONS

New online material on the basics of climate change was introduced in Autumn 2016. The multidisciplinary material has been used at several universities among students of different fields to study climate change. The multidisciplinary collaboration in climate change education is to be continued in future.

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REFERENCES

IMPACT OF AEROSOL ACIDITY AND AEROSOL LIQUID WATER ON VOLATILITY AND THE CHEMICAL COMPOSITION OF SOA FORMED FROM ALPHA-PINENE OZONOLYSIS

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Keywords: HOMs, Mass Spectrometry, Aerosol Acidity, Heterogeneous chemistry

INTRODUCTION

The largest mass fraction of atmospheric fine particulate matter (PM\textsubscript{2.5}, aerosol with aerodynamic diameters \( \leq 2.5 \) \( \mu \)m) is generally organic, dominated by secondary organic aerosol (SOA) formed from the gas-phase oxidation of volatile organic compounds (VOCs). The biogenic VOCs (BVOCs), such as isoprene and monoterpenes, are typically the most abundant SOA precursors, especially in regions of dense terrestrial vegetation. In the boreal forest, monoterpenes and especially \( \alpha \)-pinene are the major SOA precursors.

Chemical characterization of gas- and particle phase products generated from the oxidation of \( \alpha \)-pinene has been performed intensively in the last 20-30 years. These previous studies have reported the formation of oxygenated species that contribute to SOA formation. Recent development of new reagent ion chemistry, \( \Gamma \) and/or nitrate (NO\textsubscript{3}\textsuperscript{−}), for chemical ionization mass spectrometers (CIMS) have allowed for the measurement of highly oxidized multifunctional compounds (HOMs) in both gas (Ehn et al., 2014) and particle phases (Lopez-Hilfiker et al., 2016). This new class of compounds is expected to have low vapor pressure (Kurten et al., 2016) and could condense nearly irreversibly onto aerosol surfaces to produce SOA. Formation of HOMs has been proposed to occur through RO\textsubscript{2} chemistry and subsequent intramolecular hydrogen-shifts followed by rapid reaction with O\textsubscript{2} (autoxidation; Crounse et al., 2013). Formation of HOMs was then demonstrated from the oxidation of others BVOCs such as isoprene or sesquiterpenes (Krechmer et al., 2015) but also from the oxidation of anthropogenic precursors (Wang et al., 2017).

Although the formation of HOMs has been intensively studied in laboratory experiments since 2014, molecular structures and formation pathways remain uncertain. For instance, it has been suggested that RO\textsubscript{2} + NO reactions could lead to the formation of organonitrates even without suppressing autoxidation to a very large degree. In addition, the fate of HOMs remain still unknown and potential heterogeneous reactivity onto aerosol as well as photolysis can be expected. Indeed, multiphase chemistry of HOMs could be expected since recent findings have shown that oxygenated species such as epoxides (Surratt et al., 2010), organic hydroperoxides (Mutzel et al., 2015; Riva et al., 2016) and gaseous oligomers (Riva et al., 2017) undergo further multiphase reactions leading to SOA formation, highly oxidized compounds and/or volatile species. It is worth noting that recent studies have reported that oxidation of biogenic compounds in the presence of wet acidic aerosols can be an important source of SOA.

Ozonolysis of \( \alpha \)-pinene leads to formation of multifunctional gas-phase products including alcohols, hydroperoxides, epoxides and carbonyls. Such compounds can then condense onto aerosol surfaces and contribute to SOA formation. Although many previous studies have characterized the oxidation of \( \alpha \)-pinene and subsequent SOA formation, the coupled role of aerosol liquid water and acidity on the chemical composition and the physical-chemical properties of SOA remain uncertain.

In this study, we investigate \( \alpha \)-pinene ozonolysis in the presence of sulfate seed aerosol of varying acidity
and aerosol liquid water with a focus on the multiphase reactions of HOMs.

METHODS

The COALA-2 campaign was conducted at room temperature (27 ± 2°C) and atmospheric pressure in a 2-m$^3$ Teflon chamber. Experiments were carried out under steady-state conditions; meaning that a constant flow of reactants, oxidants and particles were continuously added to the chamber. Under the conditions used in this study, the average residence time in the chamber was ~ 50 min. Gaseous multi-functional organic compounds were chemically characterized using a range of long time-of-flight chemical ionization mass spectrometers (HR-LToF-CIMS) with iodide (I$^-$) and nitrate (NO$_3^-$) ionization. In addition, particle-phase was chemically characterized using Filter Inlet for Gases and AERosols (FIGAERO) coupled to an I$^-$-HR-LToF-CIMS. Size-selected ammonium sulfate aerosol particles (acidified and non-acidified) were injected into the chamber under dry (< 1%) or wet (~ 45%) conditions to evaluate the importance of multiphase chemistry in the chemical composition of the alpha-pinene-derived SOA.

RESULTS

Preliminary results obtained from COALA-2 reveal the formation of hundreds of compounds from α-pinene ozonolysis, including highly oxidized products and oligomers in both gas and particle phases. As suggested in previous studies, the largest SOA formation was observed using dry ABS seed aerosol. It is also under these conditions that the chemical composition of the particle phase was the most significantly impacted. As shown in Figure 1a, large formation of C$_8$H$_{10}$O$_x$ and C$_8$H$_{12}$O$_x$ was observed in particle phase. The concentrations of such species were also monitored in gas phase but do not present such enhancement, suggesting that the formation of the compounds identified by the FIGAERO-CIMS might be decomposition products of larger products formed within the particle phase. In addition, the C$_{18}$-C$_{20}$ dimers arising from bimolecular reactions of two peroxy radicals (RO$_2$ + RO$_2$) condense onto the seed aerosols and further react in the presence of acidic particles as revealed in Figure 1b, where the concentrations of dimers decrease after the addition of wet acidic aerosols. Although the effects of aerosol acidity and ALW on the particle phase processes of HOMs cannot be deconvoluted because water is always present in the acidified seed particles, Figure 1 suggests that aerosol acidity promotes multiphase chemistry. A smaller effect was observed for experiments performed under high-RH conditions and is attributed to dilution of aerosol acidity by additional particle water, which likely slows down the particle phase processes.

![Figure 1](466)

Figure 1. Relative abundance ([C]seed/[C]No seed) of the (a) C$_8$-monomers and (b) C$_{20}$-dimers observed in particle phase with (ABS or AS) and without (Org) seed. AS and ABS correspond to the injection of non-acidified and acidified seed aerosol under dry conditions, respectively. ABS-de/AS-de and ABS-h-
indicate the experiments performed using ABS/AS deliquesced seed aerosol into a humid chamber and ABS dry seed aerosol under high-RH conditions, respectively.

Modification of the composition of the particle phase could also impact the physical properties (e.g. volatility) of the SOA. As presented in Figure 2, the change in diameter of SOA formed in the presence of acidic seed aerosols (pink circles) is smaller indicating that the SOA formed using such seed aerosols are less volatile.

![Figure 2](VTDMA Thermograms (120 nm))

**Figure 2.** Thermograms of size-selected SOA generated from the ozonolysis of α-pinene without (org) and with seed aerosols (AS and ABS) under dry conditions.

These preliminary results indicate that certain monomers and dimers likely undergo further acid-catalyzed reactions within the aerosol phase impacting physical and chemical properties of the particle. Presence of functional groups such as hydroperoxides likely explains the large reactivity of the HOMs (Krapf *et al.*, 2016; Riva *et al.*, 2016).

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**REFERENCES**


OBSERVATION OF EVENING BIOGENIC ION CLUSTER FORMATION EVENTS IN A BOREAL FOREST

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Keywords: monoterpenes, HOMs, ion clusters formation

INTRODUCTION

Atmospheric formation of nanometer sized particles is a frequent phenomenon which significantly contributes to global aerosol particle number concentration throughout the troposphere (Merikanto et al., 2009). It results from a complex sequence of different processes including the production of clusters from gaseous precursors and the growth of these clusters to particles. Besides their effect on human health, these newly formed particles can, after they grow to larger sizes, act as cloud condensation nuclei (CCN), and impact the climate through cloud related radiative processes (Kerminen et al., 2012). Global models predict that new particle formation (NPF) could produce a substantial fraction of the total CCN budget, up to 70% in some regions (Yu and Luo, 2009), and in turn strongly control the present-day climate forcing of aerosol particles.

Benefiting from the continuous advancement of measurement techniques, our understanding of NPF has significantly improved during the last decade. For instance, state-of-the-art mass spectrometers, namely API-TOF (Atmospheric Pressure interface Time-Of-Flight; Junninen et al., 2010) and CI-API-TOF (Chemical Ionization Atmospheric Pressure interface Time-Of-Flight; Jokinen et al., 2012), have provided new insights into the identification of the gaseous precursors involved in the process. Using such techniques, evidence for the role of oxidized organic compounds (referred as HOMs, Highly Oxidized Multifunctional organic compounds) together with sulfuric acid already in the early stages of the NPF process was highlighted in several studies (eg. Schobesberger et al., 2013; Ehn et al., 2014; Bianchi et al., 2016). More recently, Kirkby et al. (2016) reported ion induced cluster formation solely from α-pinene oxidation products under atmospheric conditions in the CERN CLOUD (Cosmics Leaving OUtdoor Droplets) chamber.

Although organic nucleation at extremely low sulphuric acid concentration has been already observed in the free troposphere (Bianchi et al., 2016), the aforementioned mechanism, in which highly oxidized biogenic molecules form new particles, has never been clearly evidenced in the low troposphere. The purpose of the present work was thus to investigate the occurrence of the pure biogenic ion cluster formation in the boreal forest, using measurements performed at the SMEAR II station, where monoterpenes where previously reported to dominate biogenic emissions (Hakola et al., 2006) and produce significant amount of HOMs (Ehn et al., 2014; Yan et al., 2016). Since it was previously reported that sulphuric acid-driven pathways were dominating nucleation in Hyytiälä (Kulmala et al., 2013), the present work was rather focussed on the occurrence of “evening” ion cluster formation events, when sulfuric acid concentration is minimal.

METHODS

Measurements were conducted at the boreal SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005), during April-June 2013. Evening ion cluster formation events were detected based on the visual
inspection of the negative ion size distributions measured with a NAIS (Neutral cluster and Air Ion Spectrometer; Mirme and Mirme, 2013), with a focus on the 16:00 – 00:00 local time window, in the light of the recent work by Buenrostro Mazon et al. (2016). In order to avoid any rain related effects in the production of ions, all evenings showing evidence of precipitation after 16:00 were filtered out. The molecular composition of the negative ions was resolved with an API-TOF, and the concentration of neutral gas-phase sulfuric acid was measured with a nitrate ion based CI-API-TOF. The calibration of the CI-API-TOF was based on sulfuric acid detection (Jokinen et al., 2012).

Additional gas and ambient meteorological data, including monoterpenes (PTR-MS; Rantala et al., 2015) and O₃ (ozone analyser based on the absorption of UV radiation) concentrations, as well as global radiation (Middleton Solar SK08, Middleton Solar, Yarraville, Australia), temperature (PT-100 sensor) and relative humidity, all measured at a mast height of 16.8 m (except global radiation at 18 m), were included in the analysis. Particle size distributions measured with a Differential Mobility Particle Sizer (DMPS; Aalto et al., 2001) were finally used to calculate the condensation sink (CS), which describes the loss of vapours on pre-existing particles (Kulmala et al., 2012).

CONCLUSIONS

Consistent with previous observations at the site (Junninen et al., 2008; Lehtipalo et al., 2011; Buenrostro Mazon et al., 2016), the formation of negatively charged clusters was frequently observed within a few hours around sunset (25 evenings out of 32), as illustrated on Figure 1. In addition, we found a tight connection between the concentration of the newly formed negative ion clusters and the signal of specific classes of naturally charged monoterpenes-derived HOMs. This observation suggests a strong implication of these compounds in the ion cluster formation, while the contribution of sulfuric acid to the process appeared to be in contrast minor for most of the identified events. These results thus present the first direct evidence for the capability of biogenic HOMs to initiate the formation of atmospheric particles via an ion induced mechanism. In agreement with recent CLOUD findings (Yan et al. in prep; Lehtipalo et al, in prep), we further highlighted that ozonolysis products of monoterpenes were more efficient in forming and growing clusters than organonitrates.

During the observed events, the ion clusters only experienced a limited growth (< 6 nm) after they formed in the evening, most likely because the photochemistry and the vapours needed to sustain their growth to larger sizes were missing after sunset. The latter, however, does not preclude the chance of atmospheric clusters to reach larger diameters in a pure biogenic system when photochemical processes are active. These results rather encourage to multiple observations in order to further assess the effect of biogenic cluster formation pathways on a global scale. Getting additional insight into these processes is of great interest since they might have been a widespread source of particles and CCN during the preindustrial era; they will also most likely significantly contribute to particle formation in the future as anthropogenic emissions are expected to decrease, while the emissions of the nucleating biogenic vapours could in contrast simultaneously intensify, at least in some regions (Hantson et al., 2017).
Figure 1. Identification of an “evening” negative ion cluster formation event on 21 – 22 April 2013 using NAIS measurements. The event is seen from ~19:00 to midnight (local time) on the surface plot (A) as well as from the increase in ion cluster concentration in two size ranges, 1.5–2 nm and 2–3 nm (B).

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REFERENCES


INTEGRATED EVALUATION OF BIOGENIC SECONDARY ORGANIC AEROSOL FORMATION IN A GLOBAL CLIMATE-MODEL

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Keywords: New Particle Formation, Precursors, Global Model

INTRODUCTION

Atmospheric formation of nanometer sized particles through gas to particle conversion processes is a frequent phenomenon which significantly contributes to global aerosol particle number concentration throughout the troposphere (Merikanto et al., 2009). Besides their effect on human health, these particles can, after they grow to larger sizes, act as cloud condensation nuclei (CCN), and impact climate through cloud related radiative processes (e.g. Kerminen et al., 2012). Global models predict that new particle formation (NPF) could produce a substantial fraction of the total CCN budget, up to 70% in some regions (Merikanto et al., 2009; Yu and Luo, 2009), and in turn strongly control the present-day climate forcing by aerosol particles.

Despite the fact that instrumentation is continuously being improved, our understanding of the aerosol formation mechanism still remains uncomplete. For that reason, global models use simplistic representations of the process which are assumed to cover a large range of atmospheric conditions. Efforts have been put during the last decades to better constrain predictions to observations in the planetary boundary layer (e.g. Makkonen et al., 2009), where first attempts to describe nucleation were originally done using the binary nucleation mechanism derived from the classical nucleation theory (Spracklen et al., 2005). Parameterizations have evolved towards a more explicit description of the involvement of oxidized organic compounds from biogenic origin in the very beginning of the NPF process (e.g. Paasonen et al., 2010), as widely suggested by recent observations.

However, when evaluated against observation, the predictions of NPF and its related effects have often been discussed with respect to the choice of the parameterization for the nucleation step, while the discrepancies related to the accuracy of the predicted precursors concentrations themselves were most likely left behind further investigation. Here we report such an analysis for commonly used precursors in models, i.e. monoterpenes and their oxidation products, usually referred to as HOMs (Highly Oxygenated Molecules), as well as sulfuric acid, using simulations conducted with the global model ECHAM5.5-HAM2 (Stier et al., 2005; Zhang et al., 2012) and measurements performed at the boreal SMEAR II station in Hyytiälä, Finland (Hari and Kulmala, 2005) between 2010 and 2013.

METHODS

Monoterpene volume mixing ratios (VMRs) were measured in Hyytiälä with a quadrupole Proton Transfer Reaction Mass Spectrometry (PTR-MS), which allows real-time monitoring of VMRs down to tens of ppt. Monoterpene concentrations were derived from the signal obtained at m/z (mass-to-charge-ratio) 137 (Taipale et al., 2008). Sampling was performed close to the top of the forest canopy, i.e. 14 or 16.8 m, every second or third hour. In order to filter out extremely high monoterpene concentrations related to the activity
of the nearby sawmill, we applied the modified Thompson tau method, as previously suggested by Liao et al. (2011). Monoterpenes fluxes were calculated based on the surface layer profile method described in details by Rantala et al. (2014).

Because of the lack of continuous measurement during the whole period of interest, sulfuric acid concentration was derived from the proxy developed by Petäjä et al. (2009). The identification of NPF event days as well as the calculation of early particle growth was performed using measurements conducted with AIS (Air Ion Spectrometer; Mirme et al., 2007) and BSMA (Balance Scanning Mobility Analyser; Tammet, 2006). The contribution of sulfuric acid to the particle growth was evaluated based on Kerminen and Kulmala (2002), and organics were assumed to explain the fraction of the growth not explained by sulfuric acid. In order to get insights into CCN-like particle population, particle concentrations at larger sizes were measured using a DMPS (Differential Mobility Particle Sizer).

The ECHAM5.5-HAM2 model was run over the period of 2000-2010 using nudging technique to assimilate model meteorology towards ERA-Interim. The emissions of dust and sea salt were calculated online, while anthropogenic emissions of OC, BC and SO2 were taken from ACCMIP emission inventory. The model has been upgraded with a secondary organic aerosol (SOA) scheme including ELVOCs (Jokinen et al., 2015), and ELVOCs are participating in the nucleation of new particles (Paasonen et al., 2010). The emissions of BVOC emissions were either taken from pre-calculated fields from MACC inventory, or calculated online using MEGAN algorithm. Here we show results from online BVOC emission simulations.

Direct comparison of modelled and measured values was achieved for monoterpenes fluxes and concentrations (hourly averages), early particle growth rates (1.5-3 nm, average over event period) as well as particle concentration in the Aitken mode (hourly averages). The contributions of sulfuric acid and monoterpenes oxidation products to early particle growth were also investigated.

CONCLUSIONS

This analysis, based on a long-term dataset, allowed us to investigate how the accuracy of predicted precursors concentrations might, besides the choice of the parameterization itself, affect prediction of NPF and its effects, including especially the concentration of particles in the Aitken mode assumed to be representative of the CCN population. As shown on Fig. 1, similar seasonal trends were obtained for modelled and measured monoterpenes fluxes and concentrations over the 2010-2013 period. Best agreement was obtained between April and November, while winter time fluxes and concentrations were in contrast significantly underpredicted in the model, with consequences on the prediction of both particle growth rate and concentration. These discrepancies were identified to arise mainly from underestimated leaf area index (LAI) in the model. In the light of this preliminary results, new simulations are currently run with corrected LAI, from which better agreement is expected with observations. While participating in the identification of factors causing uncertainties in the prediction of NPF and its related effects, this work will help better constraining the process in global models.
Figure 1. Median seasonal variation of measured and modelled monoterpenes concentrations and fluxes derived from the 2010 – 2013 period. Lower and upper limits of the error bars stand for the 25<sup>th</sup> and 75<sup>th</sup> percentile, respectively. Red lines and markers indicate the monthly medians of the ratios of measured to modelled monoterpenes concentrations or fluxes.

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Clouds play a substantial role in the modification of climate. Interaction with radiation, influence on wind patterns, transportation of water and precipitation are some of their roles. The formation of ice in clouds has a major effect on their properties, especially in precipitation. Ice crystal may form either homogeneously or heterogeneously. In the former process, ice does not nucleate until -38 °C, whereas in the latter process, ice nucleates at higher temperature with the aid of aerosol seed particles. However, the impact of airborne particles in ice nucleation is poorly understood. The formation of ice in the Earth’s atmosphere is significantly influenced by various types of aerosol particles, such as mineral dusts, biological particles and carbonaceous materials. Among these ice nucleating particles, the high ability of mineral dust to nucleate ice has led this particle type to be one of the most studied agents in cloud ice and precipitation formation. There are several types of mineral dusts such as feldspar, kaolinite and illite that are revealed experimentally to be effective ice nuclei. However, the mechanism of ice nucleation of these particles is not fully understood at microscopic level. Thus, atomistic simulation can help us to investigate the microscopic mechanism of heterogeneous ice nucleation.

A recent study that used molecular dynamics simulation with all-atom water model investigated the ice nucleation in the presence of clay mineral kaolinite and it is observed that the kaolinite surface, significantly, accelerates the ice nucleation in comparison with homogeneous case. The visual inspection of ice-forming trajectories showed that the kaolinite changes the density profile of water in the second layer above its surface. This may be part of an explanation, why some mineral dusts are especially efficient at nucleating ice still remains as an open question (Cox et al., 2013) Also, ice polytype formation on kaolinite (001) surface were monitored (Zielke et al., 2016; Sosso et al., 2016). And the results of these studies are worth to consider. Kaolinite is a clay which has a layer of tetrahedral sheet of silica (SiO$_4$) and a layer of octahedral sheet of alumina (AlO$_6$) which are linked through oxygen atom. Kaolinite surface was kept fix, except the hydrogen atoms in hydroxyl groups, during the MD simulation. Ice forms on the both Al-surface which is a flexible surface and Si-surface which is a rigid one. The ice nucleus on the Al-surface is predominantly hexagonal ice $I_h$. However, for Si-surface, it is a mixture of hexagonal ice and cubic ice that is known as stacking disordered ice. This is an important point, because it shows that ice does not form on the surfaces that exactly match with either $I_h$ or $I_c$ structures. It suggests that the effective surfaces in ice nuclei should be compatible by regular arrangement of $I_h$ or $I_c$.

Studies have shown that the ice nucleating efficacy of mineral dusts is related to their specific crystallographic features. Atmospheric aerosol have different active sites and surface structures, so it is important to identify which crystallographic features and surface structures are the most efficient in ice formation, and this identification may facilitate and improve faster by using computer simulation. One of the most common groups of tectosilicate in Earth’s crust and soil cover is feldspar, so it becomes one of the important particles in ice nucleation (Pedevilla et al, 2016). In one recent study, the nature of K-rich
feldspars ‘active sites was investigated. The results indicated that the nucleation occurs on the surface patches with a special crystallographic orientation (Murray, 2017) Therefore, imperfections on surfaces, such as steps, cracks and cavities, may be responsible for higher ice nucleation efficiency. One explanation is that surface defects enhance the density of adsorbed water molecules. Thus, a molecular level study of the structures of water and ice at the interfaces of mineral dusts allows us to achieve a better understanding of this phenomenon (Kiselev et al, 2016).

METHODS

Despite numerous studies on nucleation of ice on atmospheric aerosols, this subject still needs more attention. Therefore, I will, first, use all-atom molecular dynamics (MD) simulation, using the Gromacs 5.1.2 software, to study ice nucleation in the presence of kaolinite. Water molecules will be modeled using the TIP4P/2005 potential and the CLAYFF force field is used. The Kaolinite surface is placed in the center of the simulation box as shown in the Figure 1. Lorentz-Berthelot mixing rules is used to obtain the interaction parameters between the clay and the water. The Van der Waals interaction are calculated up to 10 Å. This study helps us to obtain a precise model of the ice structure on the surface of the kaolinite. Then, I will study the role of imperfections on K-feldspars, for instance, cracks, steps and patches, in the ice nucleation. This study will help us to identify which structural materials are more efficient as an ice nucleating particle, and based on this result we will be able to suggest designs of artificial materials which are optimized for the cloud seeding application.

![Figure 1](image)

**Figure 1** Initial configuration of Kaolinite slab is in contact with the water film. Oxygen, silicon, aluminium and hydrogen atoms are colored in red, yellow, pink and white respectively.

REFERENCES


DEVELOPMENT OF SMEARCORE

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Keywords: data, software

INTRODUCTION

We are developing a new data management and analysis system SMEARCORE. A challenge in data management of SMEAR type stations is the comprehensiveness of the measurements. For example the SMEAR II station continuously measures over 1000 variables and during 2014 this produced 8 TB of raw data. The motivation behind this development is to clearly document current practices and simplify setting up new measurement campaigns and stations. We also aim to produce a high level interface to the data, which would allow independent development of further analysis and data transform tools, similar to Junninen \textit{et al.} 2009. The system will consist of three subcomponents and configuration files, see Figure 1.

- A collection component that copies data from measurement computers.
- A storage component that stores the data and indexes it.
- An analysis component which builds upon the index provided by storage.

METHODS

The idea is that end users can use the system through interfaces that represent their problem domain. When setting up measurements the user can input relevant info and metadata about measurement into a configuration file through a web interface. The configuration for that measurement then generates the required database definitions & code to transport the files between the measurement computer and the SMEARCORE server. This reduces the all too common duplication of information. For calibration and analysis code, the user would then define what data is needed and would get it in a standardized format out from the storage system. This allows the creation of generic routines that could be used at different stations for similar instruments. This also makes writing code for exporting to various other services easier, since it can also be shared between stations.

The modular design also allows us to modify the inner workings of the components, as long as the interfaces between the systems stay unchanged. This makes it easier to update the system or change it, if necessary for performance or external factors, such as licensing or hardware limitations.

CONCLUSIONS

The system is still in development. We aim to have a deployable version with the collector component ready this fall. Once the project is completed we will begin to use it alongside current implementations to test it in practice. The ultimate goal is running the data management of a future SMEAR station on the new system and being able to deploy it easily to other locations.
Figure 1: Schematic representation of the responsibilities of the different components of the system at a research station.

ACKNOWLEDGEMENTS

Work was supported by the Academy of Finland Center of Excellence programme (grant no. 307331).

REFERENCES

Atmospheric research involves several fields of science such as chemistry, physics, meteorology, mathematics, biology, agricultural and forest sciences, technology, and geosciences, combining observations, experimentation and modelling. A shift from discipline-tied fundamental education towards multidisciplinary is imperative for a successful career in climate and global change science (Nordic Climate Change Research, 2009). Based on our experience of organizing more than 50 research-intensive short courses over the past 20 years we have developed a practice supporting multidimensional learning outcomes in multidisciplinary atmospheric science courses (Lauri et al., 2016). Course practices, e.g. scheduling and principles of group division, as well as assumed learning outcomes are largely based on experience and tacit knowledge. In order to crystallize the learning outcomes for each course it is important to analyse which transferable skills the students expect to learn, how well this is realized during these course, and how useful they find the learned skills for their development as researchers. This study serves also in determining whether they the learning outcomes are constructively aligned with the teaching and evaluation methods.

INVESTIGATING STUDENTS LEARNING

We investigate the students learning expectations and experience at the ‘Winter School 2017 - Atmospheric Processes and Feedbacks and Atmosphere-Biosphere Interactions’ field course that was held 6th to 17th March 2017 in the Hyytiälä field station. Feedback was collected from the students before and after the teaching period with the aim of finding ways to improve the practices of this annually held course, as well as and other intensive courses based on a similar concept. The central task of the students on the course is was to analyze and plot data measured at the Hyytiälä SMEAR II station and Siikaneva spring 2016 campaign. The coursework was done in groups of 4-7 students and the central computational tool utilized during the course is was Matlab. Learning oral and written presentation skills was one of the learning outcomes, student groups gave three oral presentations during the course and returned a written report after the intensive period.

We investigated the expectations and assessment of learning concerning the following transferrable skills that are key learning goals in the course:

1. Data analysis skills: forming research questions for data analysis and data processing
2. Writing reports and articles: independent writing, collective writing, reviewing others’ text
3. Oral presentation skills: presenting methods, results etc. for an audience
4. Learning and teaching skills: sharing findings in a small group, sharing knowledge
5. Project and time management: working as a team, meeting deadlines

RESULTS AND CONCLUSIONS ON LEARNING

The course had 30 students, most students on their first years of their PhD studies, some master level students as well as students at the end of their PhD studies as well as post doc researchers. The students
had a background in physics, chemistry, meteorology, atmospheric science, earth science or biology/ecology and represented 16 nationalities (Bangladesh, Bolivia, China, Denmark, Estonia, Finland, France, Germany, Greece, India, Iran, Italy, Kazakhstan, Iraq, Norway and Sweden). Also the teaching staff was international 17 assistants and 11 other teachers represented 10 nationalities: Austria, China, Denmark, Estonia, Finland, Germany, Italy, Lebanon, Mexico and Russia. Half of the students were degree students at the University of Helsinki while others were enrolled in other universities and we did not find any differences in their learning expectations or experience.

The students were divided to mixed groups in terms of data-analysis skills, nationality and study field with the aim to promote peer support and horizontal learning. One student wrote “I learned how to write some coding for data-analysis, how to focus on the same topic with people with very different knowledge, what to look at when trying to comprehend natural phenomena”. The students felt that working on a joint research topic was a good way to learn data-analysis and other transferrable skills needed by researchers.

Summary of the student feedback on the course:
1. Students expected to learn transferrable skills, especially data-analysis and Matlab
2. Data-analysis skill requirements were sufficient. It was not critical for the students to know much Matlab when they start the course, but it helps and pre-course tasks should be used to support it
3. Start of Ph.D. studies or University of Helsinki master students after course “Physics and Chemistry of Air Pollution and Their Effects” is sufficient knowledge level
4. Multidisciplinary learning approach appears to be achieved and peer learning among students with different background is achieved only in some groups
5. Group working was achieved only partially, some students felt they mainly worked as individuals. Some group dynamics problems, free riding and cherry picking of tasks, were observed by the students.

Data-analysis with Matlab emerged as the most important skill, expectations of learning it were highest and the students also felt they had learned data-analysis more than the other transferrable skills. The students experienced learning of all studies transferrable skills during the 10 days at the intensive course. The learning experience lacked from the expectations most for the writing skills, which is at least partly explained by the fact that the course report had not been written by the time the after-course survey was conducted.

The course was found useful by the students and they gave a lot of improvement suggestions, indicating that they were very motivated to make it better. The feedback was condensed to concrete suggestions:
• Group division and distribution of assistants to the groups is critical and could be supported by giving different learning aims for beginner and advanced groups and giving guidance to research work in a group at the start of the course.
• Lectures at the beginning and middle of the course support getting into the topic
• Learning of time management could be supported by giving a lecture and making the students aware that they can be proactive in planning their and the groups work distribution and schedule

ACKNOWLEDGEMENTS

Research oriented intensive course concept development by Pepe Hari and Markku Kulmala is fully acknowledged. Work was supported by the Academy of Finland Center of Excellence programme (grant no. 307331).

REFERENCES

PARTITION OF DIFFERENT CO₂ SOURCES AT FOREST FLOOR IN AN EXTENSIVE TRENCHING EXPERIMENT IN A SCOTS PINE STAND IN SOUTHERN FINLAND

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Keywords: Trenching, soil respiration, roots, heterotrophic.

INTRODUCTION

Soil CO₂ emissions originate from heterotrophic respiration i.e. the decomposition of soil organic matter by microbes and autotrophic respiration from plant roots e.g. tree and ground vegetation. The different sources also interact since trees are known to allocate carbon to symbiotic mycorrhiza associated to roots (Smith and Read 2008). This sacrifice is beneficial because mycorrhiza may boost the decomposition of soil organic matter and in that way release soil nutrients for tree use.

It is suggested that even more than 50% of all carbohydrates produced by herbs per day in photosynthesis are released as CO₂ via the roots of herbs (Lambers et al. 1996), but this share in trees and the interactions with other carbon cycling processes are not quantified. It is also proposed that ericoid- and ectomycorrhizas associated with roots of different plant species (dwarf shrubs and trees) have links between each other (Villarreal-Ruiz et al. 2004). The understanding of the nature and the magnitude of the tree-related belowground carbon fluxes is needed in order to both interpret present variation in tree growth and to estimate tree growth in future.

METHODS

We established a trenching experiment at the SMEARII (Station for measuring ecosystem-atmosphere relations) in southern Finland in late 2012 with the intention to partition the different sources of CO₂ emissions at forest floor. The site is Scots pine stand (Pinus sylvestris) and soil is Haplic Podsol with soil depth of 0.5-0.7 m and intermediate fertility.

In trenching method, roots are cut and excluded from surrounding soil with impermeable fabric installed at minimum 40 cm deep ditch around a 90 x 90 cm soil plot. We used two different mesh fabrics with pore sizes 1 µm (TREN. 1 µm) and 50 µm (TREN. 50 µm) to separate the plots from the surrounding soil. Mesh size of 1 µm allows the access of water and small molecules whereas 50 µm also allows the ingrowth of mycorrhizal fungi in trenched plots, but not the ingrowth of tree roots. Tree roots were left intact in control (CONTROL) plots. In order to study the connection between different plant roots and their mycorrhizas, we applied three different ground vegetation treatments: one with intact ground vegetation (NORMAL), one with only dwarf shrubs left and herbs and mosses removed (SHRUBS) and one where all ground vegetation i.e. shrubs, herbs and mosses were cut (CUT). In total we had 9 different treatment combinations (Fig. 1) and at least 6 replicates in each combination.

Soil CO₂ emissions were regularly measured from all treatments throughout the snowless periods in 2013-2015 using manual chambers as described in Pumpanen et al. (2015). CO₂ emissions were measured on
permanently installed collars on each plot at roughly one-month intervals together with soil moisture and temperature. The decomposition rate of excised roots was determined using measured mass losses of root litterbags at each plot. Carbon emissions from dead roots in the trenched plots were calculated by these decomposition rates for smaller roots and by literature estimates for coarse roots. Unavoidably, trenching results into increased soil moisture. This effect was minimized in the analysis by first modelling the CO₂ emissions using soil moisture and temperature as inputs at each plot and then by estimating the emissions using the daily mean soil conditions at SMEAR II as inputs separately for each year.

Figure 1. The trenching and vegetation treatments with 9 different combinations. Trenching treatments included two different mesh fabrics with pore sizes of 1 and 50 µm and control without trenching. In addition, there were three different ground vegetation treatments: all vegetation removed, only dwarf shrubs left and normal intact vegetation.

PRELIMINARY RESULTS

After root-exclusion, CO₂ emissions decreased by almost 70% when all the ground vegetation was removed (TREN. 1 µm vs. CONTROL in Fig. 2 A). At the same time, CO₂ emissions from intact trenched plots decreased by about 40% but after three years, the emissions from these plots and control plots equalled (TREN. 1 µm vs. CONTROL in Fig. 2 C).

The emissions developed differently when all other plants, except ericoid shrubs were removed (Fig. 2 B). During the first two years after the tree-root exclusion, emissions were approximately 50% compared to the control, irrespective of the presence of the mycorrhizal hyphae. However, soil respiration increased notably in the third year, if fungal connection was allowed (TREN. 50 µm in Fig. 2 B).

Heterotrophic respiration comprised approximately 30%, tree roots 48%, dwarf shrubs 6% and the other ground vegetation (i.e. herbs, grasses and mosses) 16% of the total CO₂ emissions at the forest floor (Fig. 3).

The measured CO₂ emissions would have caused an overestimation by 20-45% depending on a treatment without taking into account the CO₂ emissions rising from the decomposition of the root litter and the changes in soil moisture and temperature.
Figure 2. The CO$_2$ emissions from different treatments at the forest floor in SMEARII in 2013–2015.
CONCLUSIONS

The share of tree roots comprised almost a half of all CO$_2$ emissions. The emissions developed differently when all other plants, except ericoid shrubs were removed.

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REFERENCES

DYNAMICS OF EVAPOTRANSPIRATION IN GRAZED SAVANNA GRASSLAND IN SOUTH AFRICA

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Keywords: EVAPOTRANSPIRATION, ROOT WATER UPTAKE, SAVANNA.

INTRODUCTION

The savanna ecosystems receive high solar radiation, which results in a large diurnal temperature difference between the surface and the air. They are characterized by annual precipitation that is less than the annual potential evapotranspiration. The vegetation growth in these ecosystems is, by many measures, water limited.

The variability in actual evapotranspiration (ET) affects the partitioning of available energy at the land surface, which controls many facets of land-atmosphere interactions (e.g. carbon sequestration, sensible heat flux and boundary layer height dynamics, etc…). Because vegetation is ‘first-user’ of water, ET also regulates the amount of rainfall that produces runoff and stream/groundwater recharge (Laio et al., 2001).

The savanna vegetation is characterized by coexistence of trees and grasses, which has been explained by the two-layer hypothesis. For open savannas, this hypothesis states that there exists a vertical separation between grasses and trees. This separation assumes that grasses use topsoil soil moisture whereas the trees access water from deeper soil layers, which they have exclusive access to (Ward et al., 2013).

Recent work combining in situ observations and modeling shows that maximum savanna tree abundance is negatively correlated with rainfall intensity due to difference in tree and grass water use strategies (Xu et al., 2015). This seems incompatible with the two-layer hypothesis which suggests that trees would have advantage under more intense rainfall. Wind tunnel tests with synthetic plants, show that the roles of competition for soil water and facilitation of abiotic stresses vary with spacing distance between individual plants and there exists an optimal spacing distance that lowers plant environmental stress (Trautz et al., 2017).
METHODS

This study presents eddy covariance measurements of ET from the Welgegund measurement station (26°34'10"S, 26°56'21"E, 1480 m a.s.l.) in South Africa from September 2010 to August 2016. This site is a savanna grassland with a tree cover of 15% which is grazed by cattle and sheep.

The processing of eddy covariance data was carried out according to Räsänen et al. (2017). The gap-filling of sensible and latent heat fluxes was done using an artificial neural network algorithm (Beringer et al., 2017). The input variables for the gap-filling model were incoming global radiation, vapour pressure deficit, soil moisture content, soil and air temperature and MODIS enhanced vegetation index. Soil moisture was measured at 6 levels using Delta-T PR2 probe up to 1 m depth.

To understand the dynamics of ET and root water uptake at short timescales, individual rainfall events were selected based on the precipitation time series according to Lohou et al. (2014). The rainfall events were selected as follows:

- The rainfall is preceded by 24 h without rainfall
- The rainfall event is followed by at least 24 h without rainfall
- Two consecutive rainfall events are considered one event if they are separated by less than 3 hours.
- The cumulative rainfall amount for each event must be over 3 mm.

RESULTS AND CONCLUSIONS

Figure 1 shows monthly sums of precipitation and evapotranspiration and monthly NDVI for the period ranging from September 2010 to August 2016. The mean annual rainfall was 555 mm with a standard deviation of 98 mm yr\(^{-1}\), whereas the mean annual ET was 662 mm with a standard deviation of 63 mm yr\(^{-1}\). For five measurement years, the annual sum of ET was higher than the annual precipitation. The additional water for ET can originate from trees whose rooting system is connected to groundwater.

The monthly sum of ET follows the monthly NDVI. In the year 2015 the annual sum of ET is significantly lower than the precipitation whereas in the year 2011 the sum of ET is not affected by lower rainfall (Figure 1). This is explained by a low early growing season NDVI values that appear to be due to insufficient precipitation for the grass layer development.

Sampling of the individual rainfall record resulted in 82 events within the six year measurement period. For the sampled rainfall events, the average no-rainfall recovery period was 7 days. Soil moisture measurements at the 1m depth varied by only 2% during four years measurement period. This makes it possible to analyze individual rain events (deep layer is a constant reservoir resembling a heat bath in thermodynamics), subsequent drying of the soil and root water uptake by plants. Future work will focus on estimating root water uptake for individual rain events by inverting Richards' equation.
ACKNOWLEDGEMENTS

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REFERENCES


UNIVARIATE AND JOINT BIAS CORRECTION OF TEMPERATURE AND PRECIPITATION: HYDROLOGICAL MODELLING PERSPECTIVES IN CHANGING CLIMATE

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Keywords: MULTIVARIATE, BIAS CORRECTION, CLIMATE MODELLING, HYDROLOGY

INTRODUCTION

Global (GCM) and regional (RCM) climate models are important tools for providing climate change information for hydrological impact studies. However, their direct use as input in hydrological models is hampered by errors in relation to the observed climate. To account for them, statistical tools such as quantile mapping are commonly applied when pre-processing data for hydrological models. Most of these methods, however, operate independently on the input variables, and errors in inter-variable correlations are not taken into account. For example, a correct representation of co-variations of temperature and precipitation might be important to sufficiently address climate change impacts on processes such as snow melt and accumulation around the melting point. This study addresses some questions regarding the potential benefits and shortcomings of multivariate bias correction by comparing two multivariate algorithms against traditional univariate quantile mapping. The added value of multivariate bias correction is assessed by performing hydrological simulations with bias adjusted daily mean temperature and daily precipitation as input at a high-latitude catchment in changing climatic conditions.

METHODS

Hydrological Predictions for the Environment (HYPE) is used to conduct the hydrological simulations. HYPE is a semi-conceptual, high-resolution model designed for hydrological modeling at different spatial scales (Lindström et al., 2010). The simulations were made for the upper parts of Tornio river catchment with model settings extracted from the European scale application E-HYPE. Five high-resolution (0.11° lon × 0.11° lat) GCM-RCM simulations, all run with RCP4.5 emission scenario forcing, were selected from the European branch of Coordinated Regional Climate Downscaling Experiment (EURO-CORDEX) database (Jacob et al. 2014). These simulations were used when constructing forcing data for HYPE in the present-day (1981-2010) and late 21st century (2061-2090) conditions. In addition, WATCH forcing data (WFDEI) is used as the reference data in real-world illustrations for both temperature and precipitation (Weedon et al., 2014).

Traditional non-parametric quantile mapping is applied both in delta change (M1) and bias correction (M2) mode (Räisänen and Räty, 2013; Räty et al., 2014) as the reference. The algorithm adjusts the marginal distributions of temperature and precipitation independently and the dependence structure is left mostly untouched. In the delta change mode the adjusted time series inherit the dependence structure from the baseline reference data, while in the bias correction mode the inter-variable correlations follow to a large extent the modelled one.

Two multivariate algorithms are compared against univariate quantile mapping. The first one (M3), developed by Li et al. (2014), is based on the decomposition of the joint probability distribution function (pdf) of daily mean temperature and precipitation into its marginal distributions and a copula, which
characterizes the dependence structure between the univariate distributions. As in the original paper, Gaussian copula is fitted only to the wet-day values of precipitation and temperature, while their marginal distributions are described with gamma and normal distribution, respectively. The second algorithm (M4) transforms the full pdf of temperature and precipitation towards a reference using an algorithm originally developed for image-processing purposes (Cannon, 2017). The main idea is to first randomly rotate the marginal distributions of the reference and source data to a new coordinate system, apply non-parametric quantile mapping and then map the data back to the original coordinates. When these steps are iteratively repeated a sufficient number of times, the dependence structure is shown to converge towards the reference. As the same quantile mapping algorithm is used as in the univariate case (M2), differences between M2 and M4 arise exclusively from the adjustment of inter-variable correlations.

To illustrate how these methods modify the dependence structure, examples of copula densities between daily mean temperature and precipitation are shown in Fig. 1 when adjusting one of the GCM-RCMs (direct use of model data, denoted as M0) against WFDEI. Both WFDEI and M0 indicate positive correlation between temperature and precipitation, but M0 tends to overestimate the strength of this correlation. By construction, WFDEI and M1 have identical copula density fields, while M0 and M2 closely resemble each other. Although M2 and M4 adjust marginal distributions similarly, the latter one...
modifies the copula density field to be very similar to WFDEI. However, copula densities for M3 and WFDEI show noticeable differences, even though Pearson linear correlation is similar for both, which indicates that Gaussian copula might not be the optimal model for daily temperature and precipitation.

To make inferences on the relative performance of these methods in the future climate, cross-validation based on pseudo realities is performed. In this approach, the hydrological simulation corresponding to each of the five GCM-RCMs acts at its time as surrogate for the future climate, while the rest of the N-1 simulations are used to construct bias adjusted projections for the future climate in model N. After cycling this procedure over the five pseudo realities, cross-validation statistics are calculated to measure the remaining errors in different aspects of the hydrological simulations. Here, mean absolute error (MAE) in monthly means of total runoff, evapotranspiration and snow water equivalent is shown for illustration.

RESULTS AND CONCLUSIONS

Figure 2 shows MAE for the selected variables, when averaged over the five pseudo realities, hydrological modelling domain and different months. It is seen that all methods outperform the uncorrected GCM-RCMs (M0) by large margin in the baseline period, regardless of the variable considered. By construction, M1 perfectly reproduces the reference simulations. M4 slightly improves the cross-validation statistics in comparison to M2, while M3 shows a somewhat poorer performance in comparison to the other methods, probably due to the less accurate adjustment of the marginal distributions.

The relative performance of the studied methods shows more variations in the scenario period. For total runoff, M4 marginally outperforms M1 and M2. In the case of evapotranspiration M3 and M4 have the smallest MAE, although in absolute terms the difference is rather small, even in comparison to M0. On the other hand, the delta change method (M1) has the smallest MAE in the case of snow water equivalent, which suggests that retaining the observed inter-variable (and other) correlation structures might in some cases be a safe/conservative choice when constructing future projections for hydrological purposes. One has to note, however, that snow accumulation is unrealistic for some pseudo realities because of cold biases in the corresponding GCM-RCMs, which could hamper the use of bias correction methods in these cases.
Overall, these results indicate that although multivariate methods improve inter-variable correlations of daily mean temperature and precipitation, the improvement in hydrological simulations is rather modest. However, sampling errors most likely explain part of the modest improvement, as multivariate methods require substantial amount of data for robust calibration. Furthermore, the results have been promising when M4 has been applied to higher dimensional problems (Cannon, 2017).

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INTRODUCTION

Atmospheric methane (CH$_4$) is a global greenhouse gas that is emitted to the atmosphere by both natural and anthropogenic sources (Dlugokencky et al., 2011). One of the most significant natural sources of CH$_4$ in the boreal region are lakes that mineralize carbon produced within the lake and its catchment. Majority of the CH$_4$ in lakes is formed in the anoxic lake sediment layers, although CH$_4$ can also enter lakes from the catchment by surface runoff (Miettinen et al., 2015). While sediments produce substantial amounts of CH$_4$, very small portion of it enters the water column because CH$_4$ is oxidized to carbon dioxide (CO$_2$) in the oxic sediment surface. However, the oxic layer can disappear in late summer when mineralization of organic matter consumes all oxygen from the sediment surface. Consequently, CH$_4$ is released from the sediment to the water column. CH$_4$ oxidation can also take place in the water column (Kankaala et al., 2006), but the rates and the rate controlling factors are still poorly known. To gain better understanding of the effect of bottom water anoxia on the CH$_4$ emissions from boreal lakes, we measured the CH$_4$ and CO$_2$ gas concentrations and their $\delta^{13}$C values from seasonally anoxic Lake Kuivajärvi near Hyytiälä Forest Research Station during open water season 2016. In addition, we measured the potential CH$_4$ oxidation rates in the water column after it had changed anoxic.

METHODS

Water sampling was done 4 times between May and September in 2016 at the deepest point of the lake (~12 m) (Table 1). In addition to nutrients and CH$_4$ and CO$_2$ gas concentrations, we also measured the stable isotopic signatures of CH$_4$ and dissolved inorganic carbon (DIC). The stable isotopic signature of CH$_4$($\delta^{13}$C) can be used as an indicator for CH$_4$ production and consumption because newly formed CH$_4$ has a distinctly light isotopic signature ($\delta^{13}$C = -100 to -45 ‰) (Grey 2016). When CH$_4$ is oxidized, $^{12}$C is preferred over $^{13}$C, hence the $\delta^{13}$C-value of the remaining CH$_4$ increases. Because the $\delta^{13}$C-value does not indicate how fast CH$_4$ is oxidized, we also measured the potential CH$_4$ oxidation rate by adding $^{13}$C-labelled CH$_4$ (99% $^{13}$C-label) to the samples and following the transfer of $^{13}$C label from CH$_4$ to DIC pool.

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Table 1. The sampling dates and parameters analyzed in each sampling time.
RESULTS

The stratification and bottom anoxia had developed by September and the CH₄ concentrations in the hypolimnion peaked simultaneously, indicating that during anoxia the CH₄ was not oxidized in the sediment but instead released to the water column (Figure 1a, 1c). The changes in δ¹³C-CH₄ also confirmed the transition of CH₄ oxidation zone from the sediment to the deep water column (Figure 1b).

![Figure 1. The CH₄ and CO₂ concentrations (a), δ¹³CH₄, δ¹³DIC (b), O₂ concentration, and methane oxidation rates (c) in Lake Kuivajärvi in September 2016.](image)

The potential CH₄ oxidation rates remained below detection limit until September when strong anoxia had developed in the hypolimnion (Figure 1c). Interestingly, the highest potential rates were measured right above the sediment where the O₂ concentration was the lowest (Figure 1c). Since anaerobic CH₄ oxidation taking place in Lake Kuivajärvi seems unlikely, this phenomenon could be explained by temporal micro-oxic zones allowing aerobic CH₄ oxidation in otherwise anoxic environment.

We estimated, based on the changes in the stable isotopic signature of CH₄, that in September, approximately 60% of produced CH₄ was oxidized in the water column and 40% entered the surface water layers. Even though lakes act as a source of CH₄ especially during the hypolimnetic anoxia, methane-oxidizing bacteria can still significantly reduce CH₄ emissions from lakes to the atmosphere.

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We show, using direct numerical simulations of three-dimensional incompressible Navier-Stokes equations, that there are competing interactions in a turbulent flow to transfer energy both to small as well as large scales. Under suitable modification of these interactions, which could be due to sustaining mechanism or boundaries of the flow, transfer of energy could undergo a transition in its direction [1].

Keywords: Turbulent flows, Direct numerical simulation, Energy transfer

INTRODUCTION

Energy transfer among scales is one of the key aspects of turbulent flows. The direction of the energy transfer is however determined by the conservative invariants of the dynamical system. In two-dimensions the two positive-definite invariants, energy and enstrophy, result in transfer of energy to the large scales. For the three-dimensional NSE two inviscid invariants are the energy \( E = \int d^3r \, \bar{u} \cdot \bar{u} \) and the helicity \( H = \int d^3r \, \bar{u} \cdot \bar{\omega} \), where \( \bar{u} \) is the velocity and \( \bar{\omega} = \nabla \times \bar{u} \) is the vorticity. While the energy is positive and definite the helicity could be either positive or negative therefore posing no restriction on direction of energy transfer. Helicity is known to play a key role in hydrodynamical and magnetohydrodynamical systems [2]. It is empirically observed in direct numerical simulations (DNS) of three-dimensional Navier-Stokes equations (NSE) for incompressible flows and experiments in the three-dimensional homogeneous and isotropic turbulence that energy cascades from the large forced scales to the small dissipative scales. However, there are evidences of inverse energy transfer to the large scales under special conditions. A turbulent flow confined in thick fluid layers due to formation of large scale vortex suppresses vertical motions and supports large scale energy transfer [3]. In a rotational turbulent flow with helical force both direct and inverse cascade of energy is observed [4]. Inverse energy transfer in homogeneous and isotropic turbulence was observed in a subset of interactions of the NSE with fully broken reflectional symmetry as in Ref. [5]. Presence of only homochirals (velocity Fourier modes with same sign of helicity) leads to inverse energy transfer. We show that when the relative weight between the triads formed with homochirals and triads formed with heterochirals are varied the system undergoes a criticality in the dynamics of the energy cascade and shows a transition of forward to inverse energy transfer [1]. We used the method of helical decomposition to separate the triads with homochirals from triads with heterochirals.
Figure. 1: (a) All possible triadic interactions in Navier-Stokes equations based on the helicity content of the involving Fourier modes. The arrows show the direction of energy transfer in case of one single triad. The triads with only $u^+$ (Class-I) lead to reversal of energy cascade (left). In our simulations we keep all triads of Class-I and weigh other classes of triads with a parameter $\lambda$.

**NUMERICAL METHOD**

Each Fourier mode of velocity $u(k,t)$ has two degrees of freedom as it satisfies the incompressibility condition $k \cdot u(k,t) = 0$. If we chose these degrees of freedom to be the projections on orthonormal helical waves with definite sign of helicity [6] we could write

$$u(k,t) = u^+(k,t) + u^-(k,t),$$

where $u^\pm(k,t)$ are along the complex eigenvectors $h^\pm(k)$ of the curl operator

$$i k \times h^\pm(k) = \pm k h^\pm(k).$$

We could define a projection operator

$$\mathcal{P}^\pm(k) \equiv \frac{h^\pm(k) \otimes h^\pm(k)^*}{h^\pm(k)^* \cdot h^\pm(k)}$$

such that $u^\pm(k,t) = \mathcal{P}^\pm(k) u(k,t)$. The NSE could be then independently written for each modes as

$$\partial_t u^\pm(k,t) = \mathcal{P}^\pm(k) N(k,t) + \nu k^2 u^\pm(k,t) + f^\pm(k,t)$$  \hspace{1cm} (1)

where $\nu$ is the kinematic viscosity and $f$ is the external forcing and the nonlinear term containing all triadic interactions is

$$N(k,t) = \mathcal{F}T(u^\pm \cdot \nabla u^\pm - \nabla p).$$  \hspace{1cm} (2)

**DISCUSSION AND RESULTS**

There are four classes of nonlinear triadic interactions, i.e., $k + p + q = 0$, with definite helicity signs under helical decomposition of NS equations as shown in Fig.1. Energy and helicity are conserved for each of these triads. Restricting dynamics to subsets of these triads affects the direction of the energy transfer [6, 5, 7, 8, 9]. Fully helically Decimated NSE with triads involving either only $u^+$ or $u^-$ (i.e., Class-I) shows inverse cascade of energy [5]. We introduced a parameter $\lambda$ that varies between 0 and 1 corresponding inverse energy transfer and direct energy transfer, respectively. We followed a innovative method that does not break any symmetry of the NSE and
also maintains the homogeneous and isotropic nature of the flow. We modified the nonlinear term in the following way:

\[ N_\lambda = \lambda (u \times \omega) + (1 - \lambda)[P^+(u^+ \times \omega^+) + P^-(u^- \times \omega^-)] \]  

We performed DNSs using a pseudo-spectral method on a periodic cubic domain of size \( L = 2\pi \) with resolutions of \( 512^3 \) collocation points. We injected energy at intermediate wavenumbers \( k_f \sim 10 \). We observed (see Fig. 2) the change in the sign of the energy flux occurring at about \( \lambda_c = 0.3 \) when the direction of energy transfer switches from forward to inverse. For the first time we observed a discontinuous transition in energy cascade direction. This also indicates that the turbulent flows could be considered as a out-of-equilibrium dynamical system close to criticality when \( \lambda = \lambda_c \).

References

REFILLING OF XYLEM EMBOLISM UNDER TENSION: EXPERIMENTAL EVIDENCE OF A RARE ABILITY FROM BIRCH?

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Keywords: Hydraulic conductance, Drought, X-ray microtomography, sap.

INTRODUCTION

Drought induced mortality has now been recorded in forest all over the world. The scale of the phenomenon has triggered the need to understand the process underlying tree death in case of drought. Several mechanism have been proposed (McDowell et al. 2011): 1) Hydraulic failure: cellular desiccation, cessation of symplastic biochemical and hydraulic function, and subsequent mortality after prolonged, whole-plant failure to transport water to the canopy. 2) Carbon starvation: the process by which maintenance of cellular and defensive metabolism is not met owing to low carbohydrate supply from photosynthesis and available stores; 3) Attack from biotic agent over weakened trees. While recent studies have highlighted that these three processes are likely interdependent, hydraulic failure has been the most commonly reported cause for tree death. However, trees survive most drought events and thus they must be able to restore hydraulic conductivity. While several mechanisms have been proposed (new sapwood, root pressure, etc.), a ability of trees to restore hydraulic conductance in fully embolised sapwood and particularly to do so under tension (the default situation for trees during the growing season) remains an open and critical question. We conducted a study on silver birch (Betula pendula) to test its ability to restore the ability to conduct water. Birch was selected due to its ability to refill sapwood after winter and before bud-burst during the so-called “sap season”, which shows water under positive pressure in the xylem of birches. The existence of these positive pressure in the xylem during the sap season suggests that birch have a mechanisms for sapwood refilling before the growing season, making it a good candidate to explore if refilling can also take place during the rest of the year.

METHODS

We sampled pieces of branches at different times of the year to test the tree ability to refill with root pressure. Branches were at least 16cm to avoid open vessels and let to desiccate on the bench until they were fully desiccated and not conductive, i.e. at a water potential ($\Psi$) lower than -3 MPa (Choat et al. 2012). Recovery of hydraulic conductivity of fully embolised branches was first measured in the collected samples. The recovery was induced with a small hydraulic positive pressure and it was independent of the original $\Psi$. Second, fully embolised branch segments were refilled against gravity, then against gravity in a solution of agar (-0.1MPa), i.e. under negative $\Psi$ or under tension. To test for the importance of living cells in refilling, we killed branches (in oven, wrapped to avoid cracks in wood due to desiccation). We measured changes in xylem and phloem diameters during the refilling as well as the osmolality of the first drops of sap collected from the branches after refilling.
RESULTS

No significant increase in osmolality compared to the water used for refilling was measured. Phloem show a very brief shrinkage as the xylem was put in contact with water. Then both xylem and phloem showed increased in diameter as refilling took place. Killed branches and branches from Scots pine used as controls showed no or extremely slow restoration of hydraulic conductivity. Actual xylem refilling was confirmed by x-ray microtomography (Figure 1).

CONCLUSIONS

Birch branches, provided they were still alive, were able to restore hydraulic conductivity even when fully embolised (Figure 1). Furthermore, they were able to do so under small negative water potential (i.e. small tension). Finally, our results suggest that the mechanisms underlying xylem refilling in birch is a special case of phloem unloading.

Figure 1. Cross-section under X-ray microtomography of fully embolised non-conductive birch branch, and the same branch four hours after the sapwood has been put in contact with water. Empty vessels in sapwood appear black while they look grey when water is present.

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PYROFUNGI-PROJECT HIGHLIGHTS:
THE EFFECT OF SEASON, NATURAL DISTURBANCES AND GEOGRAPHICAL LOCATION ON FUNGAL COMMUNITIES IN BOREAL FORESTS SOILS

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Keywords: BOREAL FOREST, FUNGAL COMMUNITY, PYROSEQUENCING, NATURAL DISTURBANCES

INTRODUCTION

Boreal forest soils are important in nutrient and carbon (C) cycling as these soils function as a terrestrial net sink in the global C cycling. Nitrogen (N) is typically the growth-limiting factor as most soil N is usually in forms unavailable for direct plant use. Fungi are the predominant decomposers in the boreal forests, and by forming mycorrhizal symbiosis with trees and other plants, fungi can facilitate plant nutrient acquisition from soil.

The main aim of this project was to determine for the first time the fungal community composition and to identify some of their functions in three main ecosystem stations in Finland, along a South-North transect. Further, the aim was to correlate the fungal communities with soil organic matter decomposition rates and enzyme activities. The field sites have different local treatments and research focuses: in southern Finland (Hyytiälä SMEAR II site), community structure in different soil horizons was monitored through an entire growing season, to be able to record spatial and seasonal variation. In northern Finland (Sodankylä and Värriö sites), the effect of reindeer grazing (alteration in ground vegetation) and, in north-eastern Finland (Värriö site SMEAR I site), the effect of forest fire chronosequence were studied on soil fungal communities. The powerful sequencing technology (pyrosequencing) allows detailed community analysis with relatively low labor costs. The project is therefore unique in Finland: analyses of microbial community structure and their corresponding functions have never before been combined with field monitoring data in a large scale study.
METHODS

Soil samples were collected from boreal Scots pine forest stands in close vicinity of SMEAR II (Station to measure ecosystem-atmosphere relations) in Hyytiälä (seasonal and spatial, Santalahti et al. 2016), SMEAR I in Värriö (forest fire, Sun et al. 2015), and the Arctic Research Centre of the Finnish Meteorological Institute in Sodankylä and SMEAR I (reindeer grazing, Santalahti et al. unpublished). The samples were collected in 2011 (for seasonal and spatial, and forest fire) and 2013 (for reindeer grazing).

DNA was extracted from 0.25 g (fresh weight) of soil using Mobio Power Soil DNA Isolation Kit (Mobio, Carlsbad, USA). Fungal ITS 2 regions were amplified by using fungal specific primers gITS7 (Ihrmark et al. 2012) and ITS4 (White et al. 1990) with pyrosequencing A- and B- adapters for 454 GS FLX Titanium Sequencing Platform (454 Life Sciences, Roche Diagnostic, CT, USA) and 6 bp identification tags for each sample. Pyrosequencing was conducted in the Institute of Biotechnology at the University of Helsinki. All sequence data were processed using mothur (Schloss et al. 2009) software, following a standard operation procedure (Schloss et al. 2011). Sequence data were trimmed, quality checked, aligned using pairwise alignment and clustered into operational taxonomic units (OTUs) with 97% similarity. The sequence data are available in the European Nucleotide Archive at the European Bioinformatics Institute under study no. PRJEB6382, PRJEB10726 and PRJEB21587.

To study the functional profiles of soil fungal communities in the forest fire chronosequence, the GeoChip 4.0 microarray analyses were used. The extracted genomic DNA was pooled and analyzed by Glomics Inc. (Oklahoma, USA).

To study the decomposition rate and enzyme activities, litter bags filled with Scots pine needles were buried underneath the humus horizon to the reindeer grazing study sites in Värriö in year 2014. Litter bags were harvested one year later, mass loss, moisture content and extracellular activities of organic matter degradation related enzymes were measured. For extraction of the extracellular enzymes, filter centrifugation method was utilized (Heinonsalo et al. 2012). The activities of leucine amino peptidase, β-xyllosidase, β-glucuronidase, cellulbiohydrolase I, N-acetylglucosaminidase, β-glucosidase and acid phosphatase were detected with fluorescent based assay, and for laccase colorimetric assay was used (Courty et al. 2005, Pritsch et al. 2011).

To analyze the effect of geographical location on soil fungal community, representative samples from all three study sites were selected and the sequence data of the selected samples were reanalyzed. In total, the analysis included 21 samples with 6, 5 and 10 samples from Hyytiälä, Sodankylä and Värriö, respectively.

RESULTS

In southern boreal forest in Hyytiälä, 3450 OTUs (as a proxy for fungal species) were detected from 120 samples, indicating high fungal diversity in all soil horizons, including also the deeper mineral horizons. The diversity decreased with soil depth. Seasonally, Basidiomycetous ectomycorrhizal (ECM) fungi dominated the communities during the growing season and Zygomycetous saprotrophs (SAP) dominated the communities in March under snow cover. Spatially, SAP fungi dominated the upper most raw litter layer, whereas ECM fungi dominated deeper soil horizons.

In forest fire study in subarctic boreal forest soil in Värriö, over 2000 fungal OTUs were detected from 50 samples, indicating again high fungal diversity. Community composition in the different aged fire areas were different and the functional gene pool correlated positively with fungal OTU richness. Fungal diversity was highest on the youngest site where the fire had occurred 2 years ago and the fungal diversity decreased on sites with time since the fire.

In reindeer grazing study in northern and subarctic boreal forest soils in Värriö and Sodankylä, 1186 fungal OTUs were detected from 38 samples, corroborating the above observations of high fungal
diversity in soil. Overall, reindeer grazing had no clear effects on fungal diversity or richness estimates, but changed the soil fungal community structure. Further, grazing related vegetation changes also explained the variation in the fungal community structure. Grazing also affected SOM degradation related enzyme activities. In general, the enzyme activities were higher in the grazed sites compared to non-grazed sites, except for laccase, which was higher in the non-grazed sites. This indicates a potential for long-term changes in the soil organic matter decomposition rate resulting from grazing.

The reanalysis of the sequence data based on geographical location revealed 909 OTUs from 21 samples. The species richness was significantly higher in southern boreal forest in Hyytiälä than in northern and subarctic boreal forests in Värrö and Sodankylä. Hyytiälä also harboured the highest number of unique OTUs. There were no differences in diversity and evenness across the locations. Each location harboured unique communities that clustered together based on the sampling site in Principal Coordinates Analyses (PCoA).

CONCLUSIONS

Our analyses revealed that the fungal communities are species-rich across the climatic gradient. The fungal communities were highly variable and stratified by depth and geographic location in boreal forest soils. The fungal communities shifted drastically and rapidly in time: in late winter dominated SAP fungi were replaced by ECM fungi during the growing season. Despite of observed functional redundancy in the subarctic site, the fungal community richness and functional gene diversity correlated positively, indicating that higher microbial diversity in soil supports higher genetic potential for maintaining crucial biochemical reactions in soil. Overall, reindeer grazing had significant effect on the soil fungal community structure and SOM degradation related enzyme activities. With longer time scales, grazing may affect SOM decomposition through changes in fungal communities and their corresponding enzyme activities. Based on our studies, although different natural disturbances may affect fungal communities and their composition, the core communities remain largely unaffected. The effect is most drastic immediately after the disturbance, but the soil fungal communities have the ability to recover quickly.

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TEMPORAL VARIATION OF VOC FLUXES ABOVE A BOREAL FOREST

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Keywords: PTR-TOF, eddy covariance, exchange, flux.

INTRODUCTION

Boreal forests cover around 30% of the world’s forest area and their emissions have an important impact to the air quality and air chemistry of the northern atmosphere. They exchange mainly water vapor and CO₂ with the atmosphere. In much lower amounts, various volatile organic compounds (VOCs) are emitted, which fulfill various functions, e.g. plant communication, stresses protection (e.g. O₃, heat, herbivores) or by-product of the plant metabolism (Mogensen, 2015 and references therein). The emissions oxidize to form aerosol or grow existing aerosols, which can then act as cloud condensation nuclei and form clouds, which can influence the global climate. In this study we determine the VOC exchange of a boreal forest during measurement periods in April, May and June 2013.

METHODS

A proton transfer reaction time of flight mass spectrometer (PTR-TOF 8000; Ionicon Analytic GmbH) was used to measure VOC spectra with 10 Hz from 23 m above the ground. Together with the vertical wind data, fluxes were calculated using the eddy covariance method. The measurements were conducted on a scaffold tower (61.847407°N, 24.295150°E) above the boreal forest at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) in Hyytiälä, Finland and lasted from April to June. The trees are 18 m high and the main tree species are Pinus sylvestris (Scots pine) and Picea abies (Norway spruce).

RESULTS & CONCLUSIONS

The measurement periods in April, May and June 2013 were chosen to represent the snowmelt, start of the growing season and summer, respectively. During the campaign 22 VOCs with exchange were found. Butene & butanol was the only compound which was identified as being anthropogenic, while the remaining compounds were biogenic. The emissions increased from spring to summer, following the increase of temperature and photosynthetically active radiation. The number of compounds with exchange also increased with three in April to 12 in May and, 19 in June. In Fig. 1 the nine most emitted compounds during the measurements and their relative contribution to the total 24h emission are shown.

During the snowmelt, the average 24h emission was 0.68 nmol m⁻² s⁻¹. Anthropogenic emissions of butene & butanol dominated, comprising over 60% of the emissions. The sum of monoterpenes and acetone were the only other two emitted compounds in April, contributing each around 20% to the emission.

At the start of the growing season the situation changed, biogenic emissions are emitted more strongly. This can be seen in the rise of the average 24h emission to 1.39 nmol m⁻² s⁻¹. Methanol was the most emitted compound (35%), followed by the monoterpenes (23%) and acetone (17%). The relative influence of butane & butanol to the total emission decreases (11%).
In summer the highest total emission, 3.12 nmol m\(^{-2}\) s\(^{-1}\), was recorded. The order of the most emitted four compounds was similar as in May. Methanol (39%) had the highest emissions, then came the monoterpenes (19%), acetone (13%) and butene & butanol (8%). Even though the relative contribution to the total emission of the top four compounds may have decreased, all of their emissions increased.

![Pie charts showing composition of total emissions from April, May, and June.](image)

Figure 1: Composition of the total emissions from April (left), May (middle) and June (right) 2013.

Overall, the measurements at SMEAR II identified the most emitted VOCs and their temporal behaviour. Furthermore, the anthropogenic emissions of butene & butanol were measured for the first time in Hyytiälä. With the increase of the biogenic emissions, the influence of the anthropogenic fluxes to the total emission decreases. Over 75% of the emissions were comprised by the four most emitted compounds. However, the compounds with flux showed a high diversity, 12 of the 22 measured compounds were just detected in one of the periods. More detailed information can be found in Schallhart et al. (2017).

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REFERENCES


QUANTIFYING PHYSICAL PROPERTIES OF ORGANIC AEROSOL THROUGH DESORPTION THERMOGRAM MODELING

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Keywords: ORGANIC AEROSOL, DESORPTION, OLIGOMERIZATION, VOLATILITY.

INTRODUCTION

One of the most important constituents of atmospheric aerosol particles is organic matter, making up 20% to 90% of the mass of sub-micron particles, which play a climate-critical role as cloud condensation nuclei (CCN) (Lee et al., 2013). A large fraction of organic aerosol is formed from gas-phase precursors (secondary organic aerosol, SOA), which are typically produced by oxidation of volatile organic compounds, such as isoprene and monoterpenes. Gas-to-particle conversion of such compounds explains 90% of new particle growth to CCN within the boundary layer (Riipinen et al., 2012).

Atmospheric models have underpredicted observed SOA loadings when using traditional descriptions of SOA growth (e.g. Heald et al., 2005; Dzepina et al., 2009), i.e. assuming equilibrium partitioning between gas and particle phase based on the volatility of the involved organic molecules. Also, the application of partitioning theory to SOA growth experiments infers volatility distributions that overestimate SOA evaporation (Vaden et al., 2011). These failures of equilibrium partitioning modeling efforts may be due to inaccurate descriptions of gas-phase radical chemistry or multiphase accretion chemistry, or invalid assumptions of particle phase state (e.g. Ehn et al., 2014; Surratt et al., 2006; Virtanen et al., 2010), or a combination of these issues. Recent studies have suggested that oligomerization in SOA needs to be considered for accurately predicting SOA physical properties. Oligomer formation is believed to take place within minutes upon SOA formation, and oligomer decomposition may indeed control SOA evaporation rates (Roldin et al., 2014; Kolesar et al., 2015b).

Various mass spectrometric techniques have been developed to provide relatively non-invasive methods of measuring the molecular composition of organic aerosol, thus allowing for characterizing oligomers (e.g. Beck and Hoffmann, 2016), and some of them directly connecting them to aerosol physical properties (e.g. Faulhaber et al., 2009; Yatavelli et al., 2012). A recently developed technique is the Filter Inlet for Gas and AEROsol (FIGAERO) that is coupled to a high-resolution time-of-flight chemical ionization mass spectrometer (CIMS) (Lopez-Hilfiker et al., 2014). Using iodine as a reagent ion, the molecular composition of a major fraction of an organic aerosol sample can be measured as it desorbs during controlled heating (Lopez-Hilfiker et al., 2016). The result is a set of thermograms (signal from desorbing compounds vs. ramped temperature), one for each composition. When sampling ambient SOA, as well as for SOA generated in the lab from α-pinene oxidation, the thermograms for many compositions typically show that a substantial fraction of material is desorbing at temperatures that suggest a much lower volatility than the volatility expected from the detected elemental composition (Lopez-Hilfiker et al., 2015; Lopez-Hilfiker et al., 2016). These findings support the hypothesis that oligomer formation and decomposition are playing a key role in determining SOA properties. Some very recent studies have tried
to improve our understanding of which SOA properties determine the observed FIGAERO thermogram shapes (overall or compound-specific), through detailed analysis and instrument comparison (Stark et al., 2017) or through dedicated sets of chamber experiments (Huang et al., 2017). However, a more systematic approach is still outstanding.

For our study, we have developed a detailed model of the temperature-controlled evaporation of organic aerosol in the FIGAERO. The goal is to understand on a yet unattained systematic level, which properties of organic aerosol components determine the shapes of the thermograms. We apply the model to FIGAERO measurements of SOA that was formed in chamber experiments from the oxidation of monoterpenes (α-pinene and Δ3-carene), with the expectation that we can quantify the kinetics that govern the formation and decomposition of oligomers, as well as physical SOA properties that may affect certain aspects of the observations.

**METHODS**

We have developed a model to describe the signal obtained from the particle-phase measurements using the FIGAERO-CIMS. The modeled processes are the desorption of molecules from an aerosol (or solution) sample, previously collected (or injected) onto a PTFE filter, while exposed to a flow of clean N2, as well as subsequent transport of these molecules into the CIMS. The N2 flow was usually heated, with its temperature ramped linearly from room temperature up to 200 °C. A detailed description of the method is provided in Lopez-Hilfiker et al. (2014). A variety of experiments aided in determining model parameters, such as thermal desorptions following the direct injections of calibrant solutions onto the filter, and isothermal desorption experiments. Eventually, we have been applying the model to well-controlled SOA formation experiments conducted during intensive measurement campaigns at the Pacific Northwest National Laboratory’s 10.6 m³ environmental chamber (e.g. D’Ambro et al., 2017).

The desorption for molecules of a certain compound i, present in a deposited aerosol particle, is described by the Hertz-Knudsen equation (Cappa et al., 2007). The rate of desorption is therefore mainly dependent on the compound’s absolute vapor pressure (C*), an evaporation coefficient (α) and the condensed phase surface area. Corrections are applied for the Raoult effect and for diffusion limitations both within the particle and into the gas-phase. Two additional terms describe the production of molecules of compound i in the particle by oligomer dissociation, and their loss by oligomer formation. The terms are inspired by Kolesar et al. (2015a) and are temperature-dependent as in Arrhenius’ equation. As desorbing molecules need to travel through the collection filter, before they can be measured, we account for consequent vapor-surface interactions in a fashion similar to how Zhang et al. (2014) treated the reversible loss of vapor compounds to PTFE laboratory chamber walls.

**RESULTS & CONCLUSIONS**

Our model generally obtains thermograms similar to the observations by FIGAERO-CIMS. A key for this achievement is the inclusion of vapor-surface interactions in the model, with the governing parameters being a time scale τ and an equivalent wall organic aerosol concentration Cw. Only then, the gradual downslope towards higher temperatures is obtained, which is observed in all experiments, even for the injection experiments when particle properties are irrelevant and oligomerization not expected. We determined τCw to be on the order of 5 mg m⁻³ s, in agreement with previous studies of the interactions of organic vapors with PTFE surfaces (Matsunaga and Ziemann, 2010).

In the absence of oligomers, the factors that mainly determine the peak position are: particle-phase diffusivity, expressed as a reduction in α (e.g. Saleh et al., 2013), C*, and the enthalpy of vaporization ΔH. The latter also affects the steepness of the peak’s slope and hence width. The modeled peak position is sensitive to both C* and ΔH. Using literature values for C* and ΔH for various carboxylic acids, and α = 1, we obtain model thermograms that agree well with measurements following injection of these acids onto the filter (Lopez-Hilfiker et al., 2014).
When sampling SOA however, the corresponding thermograms usually exhibit an initial peak, followed by a shoulder towards higher temperatures, or even a second peak (Lopez-Hilfiker et al., 2016). Using our model, we are able to simulate also these more complex thermogram shapes when including the oligomerization terms (Figure 1). The rate constants and activation energies that control oligomer formation and dissociation used as free fitting parameters.

For efficiently fitting all free parameters, we are adopting state-of-the-art optimization algorithms. By fitting to the observed thermograms of the individual SOA molecular compositions, we are gaining quantitative insights into the dynamics of the reversible oligomerization reactions occurring in SOA.

Figure 1. Thermogram for C₈H₁₂O₅ desorbing from SOA (black), and corresponding model fit (red).

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INTRODUCTION

Forestry and agriculture are the major bioenergy sectors in Finland. Intensive forest harvesting techniques are being used in Finland to enhance the share of bioenergy in the total energy consumption (Hyvönen et al., 2016). However, there are no clear indications as to how environmentally safe are these intensive forestry practices in Finland. We address this issue in the INDO-NORDEN project through field studies assessing the climate impacts on the ecosystem carbon and nitrogen balance and detailed life cycle assessment. To understand the role of agriculture in the Finnish bioeconomy strategy, we follow a holistic field experimental approach addressing several major issues relevant to Nordic agriculture under changing climatic conditions. There is a considerable potential for process integration in the biofuel sector (Binod et al., 2010; Raud et al., 2015). INDO-NORDEN plans to develop biofuel production processes adopted in Estonia and India with a major aim of enhancing biofuel yields. Additionally, the effects of biomass raw material on ash characteristics and behavior as well as on the fine particle and gas emissions in biomass-fired combustion plants will be evaluated.

INDO-NORDEN PROJECT METHODOLOGY

Finland, Estonia and India have joined hands in ERA-NET cofounded project with the broader objective of addressing bioenergy issues in all forms of biomass (solid, liquid, and gas – Figure 1) as relevant to the participating countries. Finland addresses land use aspects of biomass production in forestry and agriculture. For the purpose, two research sites are currently operational – one in Maaninka, 40 km from Kuopio in Eastern Finland and another one in Hyytiälä in central Finland. The Maaninka site is located close to a biogas plant at the Luke research station. This biogas plant will utilise farm waste as well as a part of the harvested legume crop for anaerobic digestion. The impact of incorporating N-rich legume biomass on the biomethan yield will be assessed. India and Estonia will deal with processes involved in bioethanol and biobutenol production from agricultural residues available in their respective countries.

At the Maaninka site, the focus is on agriculture with red clover and grass mixture cultivation on a mineral soil (Figure 2). The objective of the study here is ascertain if the cultivation of a perennial legume crop (red clover) with forage grass leads to lowering of N\textsubscript{2}O emissions and thus supports better grassland principles. Eddy covariance (EC) measurements of net ecosystem CO\textsubscript{2} exchange (NEE) and N\textsubscript{2}O exchange from the site are ongoing. A Gill R3-50 sonic anemometer for wind velocity components, a LI-7000 infrared gas analyser for CO\textsubscript{2} and water vapour density and a pulsed wave quantum cascade laser spectrometer for N\textsubscript{2}O, CO\textsubscript{2} and water vapour density are being employed to generate data at a 10 Hz frequency, Supporting soil, plant and meteorological data are being collected.
At the Hyytiälä site, the focus is on forest management issues. Intensive forest harvesting practices for bioenergy production are in practice in Finland. What is the impact of such intensification practices on the environment? Such questions are largely unanswered. For the purpose, we have established an EC site on a clear-cut forest close to the SMEAR II station. The standing forest at the station serves as the reference case, while the clear-cut EC measurements will represent the impact of clearing a standing forest. Chamber GHG measurements from locations with and without residues at the site will highlight the impact of removing harvest residues. Measurements and data processing are still ongoing. Therefore, we present here some preliminary results on the NEE of legume grass mixture cultivated at the Maaninka site (Figure 3)

CONCLUSIONS
Eddy covariance measurements of NEE and N₂O exchange began in early May when the snow at the site had thawed in the spring. The perennial red clover and grass mixture that was sown in 2016 started its regrowth during this period. The crop was fertilised in late May. First harvest of the crop was performed in early July and the second harvest in late August. The NEE was close to zero early in the season. With increasing temperatures and radiation levels, the grass mixture enhanced its photosynthetic activity to reach a peak in early June. The crop continued to sequester atmospheric CO₂ until early July, when the crop was harvested for the first-cut biomass. The impact of this harvesting is evident in the NEE data shown in Figure 3. Soon after the crop harvest, the crop turned into a source of CO₂ temporarily. The crop was fertilised with N fertilisers after the first-cut. With temperatures, soil moisture and PAR levels being favourable and with soil high, the crop mixture began to produce tillers thus allowing a vigorous plant growth with a peak in the third week of July. The second-cut was performed during late August when the peak crop growth had plateaued. Soon after the second harvest, NEE declined sharply. Based on the data presented in Figure 3, on a seasonal basis, the crop accumulated more CO₂ than the amount the whole ecosystem released to the atmosphere. Further data analyses detailing the factors governing NEE, N₂O exchange and complete life cycle analysis of the crop production system are yet to be performed.

ACKNOWLEDGEMENTS

We acknowledge the funding support from the Academy of Finland (project no. 311970 – Holistic processes and practices for clean energy in strengthening bioeconomic strategies [INDO-NORDEN]). We thank the excellent field support by the technical staff of the SMEAR station in Hyytiälä. The financial support from the Centre of Excellence in Atmospheric Science - From Molecular and Biological processes to The Global Climate, University of Helsinki is acknowledged.

REFERENCES


THE IMPACT OF PLANT-DERIVED CARBON FLOW ON FUNGAL AND BACTERIAL COMMUNITIES

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Keywords: Boreal forest soils, fungal community, bacterial community, functional gene pool.

INTRODUCTION

The boreal forests form globally stable and large carbon pools. In the organic layers of boreal forest soils, carbon is stored in the form of complex polymers including phenolic and humic compounds. The humus layer in boreal forest soils is typically dominated by ectomycorrhizal fungi which are shown to be able to break down organic matter in order to acquire nitrogen from the complex substrates (Lindahl & Tunlid 2015).

In boreal forest ecosystem, ectomycorrhizal and saprotrophic fungi are suggested to compete for the same substrate (Gadgil & Gadgil 1971, Fernandez & Kennedy 2016). The Gadgil theory proposes that ectomycorrhizal fungi outcompete the saprotrophs by suppressing their growth and inhibiting their functions due to the carbon flow provided by the plants (Gadgil & Gadgil 1971). Based on this theory, saprotrophic fungi would start to dominate the fungal community when the plant-derived carbon flow is restricted.

Changes in fungal and bacterial communities are interlinked with each other. Different mycorrhizal fungi may harbour different bacterial populations (Timonen et al. 1998). It has been suggested that mycorrhizal fungi shape associated bacterial community by carbon and nutrient flows (Izumi & Finlay 2011). In turn, the bacteria may assist mycorrhizal fungi in several functions for example by fixing nitrogen (Nguyen & Bruns 2015).

In this current study, we investigated in three-year field experiment whether the restriction of photosynthetic carbon flow from the plant favor saprotrophs or other fungal opportunists in the humus. Further, we hypothesized that change in fungal community composition trigger changes also in the bacterial community structures.

METHODS

The field experiment was conducted at Hyytiälä forestry field station (SMEAR II, University of Helsinki) in southern Finland. To discriminate the photosynthetic carbon flows, bags filled with sieved (4 mm) and homogenized humus were buried between organic and mineral soil horizons. The photosynthetic carbon fluxes were restricted with three different mesh sizes of the bags, 1 µm, 50 µm and 1 mm. These
DNA was extracted with NucleoSpin Soil DNA extraction kit (Macherey-Nagel GmbH & Co) and further purified using a PowerClean Pro DNA Clean-Up kit (MoBio Laboratories) according to the manufacturer’s instructions. The fungal and bacterial community structures were determined with next generation MiSeq Illumina sequencing at the Institute of Biotechnology (University of Helsinki) using gITS7 and ITS4 -primers for fungi and f341 and r785 -primers for bacteria (Ihrmark et al. 2012, Klindworth et al. 2013). Potential functionality of the microbial community was investigated with DNA-based GeoChip 5.0 (Glomics Inc).

The sequences obtained from MiSeq were further cleaned, trimmed, assigned to operational taxonomic units (OTUs) and aligned against UNITE database for fungal sequences or against SILVA database for bacterial sequences using mothur (Schloss et al. 2009). The differences in the microbial community structures between the treatments were further analysed with R program (R Core Team 2016). The fungal OTUs were assigned to functional guilds with FUNGuild database (Nguyen et al. 2016).

MAIN RESULTS & DISCUSSION

Both the bacterial and fungal community structures between the 1 µm and 1 mm mesh bags differed from each other (p ≤ 0.05) whereas the communities in the 50 µm mesh bags did not differ from other mesh sizes. However, treatment did not cause statistically significant change in the soil organic matter degradation related gene pools assayed with GeoChip. However, since the soil organisms can have different metabolic activities in their life cycle (Blazewicz et al. 2013), and since microbial communities inside the different mesh bags had different effects on the extracellular enzyme activity and soil organic matter profiles (Adamczyk et al. unpublished), the expression of the genes as well as amount and activity of the produced enzymes might have differed highly between the treatments.

The abundances of ectomycorrhizal Suillus and Piloderma as well as soil saprotrophs Mortierella and Trechispora differed with statistical significance between the 1 µm and 1 mm mesh treatments. From these Trechispora was more abundant in 1 µm treatment whereas others were more abundant in 1 mm mesh bags. Likewise, nitrogen fixing bacteria harbouring order Rhizobiales was with statistical significance more abundant in 1 mm mesh treatment than in 1 µm mesh. Although these bacteria can exist in the soil as free-living organisms, they are frequently associated with ectomycorrhizal root tips, and they have been proposed to participate in the soil nitrogen cycling by fixing nitrogen and providing it to both the mycorrhizal fungus and the host plant in the exchange for carbon (Nguyen & Bruns 2015).

Overall the abundance of saprotrophic fungal guilds declined during the three-year experiment in the 1 µm mesh bags while in the 1 mm mesh bags their abundance stayed the same. According to the hypothesis based on the Gadgil effect, the amount of saprotrophs was expected to increase in the 1 µm mesh treatment. However, the Gadgil effect has been previously proven mainly on plant-derived litter substrate, and was not visible in latest study conducted in boreal forest ecosystem with humus as a substrate (e.g. Bödeker et al. 2016), and they have proposed that the Gadgil effect might take longer time to occur in the humic substrates than in litter. Further, it has been speculated that the Gadgil effect is affected by several mechanisms other than exclusion of plant carbon flow. These mechanism are for example the availability of soil nitrogen, soil moisture content, soil pH, and increase of labile carbon input to soils due to the disturbance of the treatment (Averill & Hawkes 2016, Fernandez & Kennedy 2016). Moreover, the ability of ectomycorrhizal fungal community to degrade soil organic matter may influence the outcome of competition between saprotrophic and mycorrhizal fungi.
CONCLUSIONS

We studied in three-year field experiment the effect of restricted photosynthetic carbon flow from the plant to the soil fungal and bacterial communities’ composition and their potential functionality. We observed the restriction on direct carbon flow to cause changes in the community structures of both bacteria and fungi, but our data did not support the Gadgil theory.

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REFERENCES

THE RELATIONSHIP BETWEEN PLANETARY BOUNDARY LAYER HEIGHT AND DIFFERENT RADIATION VARIABLES

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Keywords: planetary boundary layer height, radiation, lidar.

INTRODUCTION

The planetary boundary layer (PBL) is the lowest part of the troposphere. It is directly influenced by the presence of the underlying Earth’s surface. The boundary layer processes control the exchange of energy, momentum, water and trace substances between the Earth’s surface and the free atmosphere (Seidel et al., 2010). The height of the planetary boundary layer (PBLH) depends strongly on the stability of the atmosphere and it can vary from less than one meter to few kilometres during diurnal and seasonal cycles. The PBL has significant impacts on climate, weather and air quality.

The structure of the PBL is largely influenced by land surface processes. These processes include absorption and emission of radiation, heat energy transfer between the atmosphere and soil and mechanical processes (Dang et al., 2016). For example, the heating of surfaces creates a forcing for thermal convection, which changes the structure of the PBL. In this study we focus on the relationship between different radiation variables and the PBLH. Our aim is to create a proxy for estimating the PBLH using these radiation variables and possibly other common meteorological variables.

METHODS

The data used in this study is from SMEAR II station (Hari & Kulmala, 2005). The station is located in a rural boreal forest area in southern Finland. The PBLH is retrieved from Doppler light detection and ranging (lidar) instrument. It measures the vertical profile of backscattering from aerosols with high temporal resolution. The aerosol concentration is much higher in the PBL than in the free atmosphere. The gradient of aerosol concentration can be used to determine the PBLH as the backscattering signal decreases most rapidly at the top of the boundary layer (Dang et al., 2016).

Table 1 shows different radiation variables measured at the SMEAR II station between years 1997 and 2017. The correlation between different radiation variables and the PBLH are calculated to better understand how these radiation variables effect the development of PBL. A previous study done by Dang et al., (2016) shows that the strongest correlations between daytime lidar-derived PBLH were observed with upward long wave radiation, surface temperature and surface sensible heat fluxes with correlation coefficients between 0.63-0.72. In this study we will also look at the time series of radiation data and time series of ratios of different radiation data in order to investigate potential changes in cloud cover. The proxy to determine the PBLH will be calculated as a function of commonly measured radiation variables and other meteorological parameters such as temperature and relative humidity.
Table 1. Different radiation variables measured at the SMEAR II station in Hyytiälä, Finland, between years 1997-2017. The blue bars indicate the time when a particular variable was continuously measured. The variables which are mentioned several times have been measured at different locations at the station.

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EXTRA-TROPICAL CYCLONES IN THE FUTURE: IDEALISED CLIMATE CHANGE EXPERIMENTS WITH OPENIFS

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Keywords: CLIMATE CHANGE, EXTRA-TROPICAL CYCLONES, OPENIFS, PRECIPITATION.

INTRODUCTION

Extra-tropical cyclones constitute a large part of the atmospheric circulation in the mid-latitudes. Many high-impact weather events are also associated with extra-tropical cyclones and in the mid-latitudes extra-tropical cyclones are responsible for at least 80% of precipitation (Hawcroft et al., 2012). There are many studies which attempt to identify how the number or location of extra-tropical cyclones will change in the future as the climate warms. Climate models predict a poleward shift of the storm tracks (regions of enhanced extra-tropical cyclone activity), a slight decrease in the total number of extra-tropical cyclones and potentially a small increase in the number of extreme extra-tropical cyclones. However, such future predictions are somewhat uncertain, especially in the North Atlantic where the current generation of climate models struggle to reliably reproduce the current day distribution of extra-tropical cyclones. Consequently, it is even harder to extract reliable information about how the structure of extra-tropical cyclones will change in the future. For example how will the spatial patterns of precipitation and the strongest winds change?

METHODS

The global atmospheric model, OpenIFS, is used in this study. OpenIFS is a version of the full Integrated Forecast System (IFS) which is used operationally at the European Centre for Medium Range Weather Forecasts (ECMWF). The IFS is currently the world’s most accurate global weather forecast system. The IFS consists of a weather prediction model, a wave model, and a state-of-the-art data assimilation system. OpenIFS has exactly the same atmospheric dynamics and physical parameterizations as the full IFS but does not include the data assimilation system. OpenIFS is made freely available to Universities and research institutions under license.

In this study, we configure OpenIFS into a highly simplified set-up: an aqua-planet. In an aqua-planet, the surface of the Earth is all ocean and idealised, zonally uniform distributions of sea surface temperature (SST) are specified. The incoming solar radiation is fixed at March equinoctial values causing there to be no seasonal variation and resulting in both hemispheres being the same. Given the absence of land masses, mountains and any zonal variations means that the jet streams and storm tracks in an aqua-planet are zonal and continuous around the globe. Extra-tropical cyclones still develop and resemble realistic weather systems.

Two experiments are conducted with OpenIFS. In the control simulation the SSTs are specified according to the QObs SST distribution (Neale and Hoskins, 2000). In the sensitivity experiment, designed to be a pseudo-climate change experiment, all SSTs are uniformly warmed by 4 K. The meridional temperature gradients are the same in both experiments. Both experiments are run for
11 years however the first year of simulation is excluded to prevent any potential model spin-up issues. The simulations have a horizontal spectral resolution of T159 (equivalent to 125 km) and have 61 vertical levels. Output is written every 6 hours to enable cyclones to be tracked.

From the model output, the zonal mean climatology of the zonal wind component, potential temperature and precipitation are compared to assess how the 4 K warming alters the basic circulation patterns. In addition, an automated tracking algorithm, TRACK, is applied to the output data to identify and track all extra-tropical cyclones. TRACK identifies localized maxima in the 850-hPa relative vorticity truncated to T42 spectral resolution. Only extra-tropical cyclones which have relative vorticity values exceeding $1 \times 10^{-5}$ s$^{-1}$, travel at least 1000 km and exist for at least 2 days are retained to ensure that only large-scale mobile extra-tropical cyclones are considered. From the TRACK output, the basic climatologies (e.g. number and intensity distribution) of the extra-tropical cyclones are compared between the two different experiments.

The structure of the extra-tropical cyclones in the two different experiments are compared by creating mean cyclone composites following the method of (Catto et al., 2010, ) and (Dacre et al., 2012). For each experiment, the 200 strongest extra-tropical cyclones (in terms of their maximum 850-hPa relative vorticity) are identified. Next the the position of each cyclone at different offset times relative to the time of maximum vorticity (e.g. 24 hours before) is determined. Next a radial coordinate system with a radius of 12 degrees is defined and centered on each cyclone center at each offset time. A range of variables (e.g. precipitation, mean sea level pressure etc.) from the OpenIFS gridded output are then interpolated onto this radial grid. The cyclones are rotated so that all travel due east and then the variables on the radial grid are averaged. The composite extra-tropical cyclone is the simple arithmetic mean of the 200 individual, rotated ETCs.

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>SST + 4K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>3496</td>
<td>3338</td>
</tr>
<tr>
<td>Mean vorticity</td>
<td>6.19</td>
<td>6.25</td>
</tr>
<tr>
<td>Median vorticity</td>
<td>6.00</td>
<td>5.98</td>
</tr>
<tr>
<td>Vorticity standard deviation</td>
<td>2.52</td>
<td>2.65</td>
</tr>
<tr>
<td>Maximum Vorticity</td>
<td>15.53</td>
<td>17.08</td>
</tr>
<tr>
<td>200 Threshold</td>
<td>10.44</td>
<td>10.70</td>
</tr>
</tbody>
</table>

Table 1: Statistics of extra-tropical cyclones identified in the control and SST + 4K experiments by TRACK. Vorticity values are for 850-hPa relative vorticity and have units of $\times 10^{-5}$s$^{-1}$

RESULTS

Warming the SSTs by 4 K results in a notable increase in the zonal mean tropical precipitation, from approximately 11 mm day$^{-1}$ to almost 14 mm day$^{-1}$. Smaller increases are observed in the extra-tropics and the extra-tropical peak in the zonal mean precipitation moves polewards by about 6 degrees latitude. The jet streams also move poleward and the jet maxima move upwards when the SSTs are warmed. This is consistent with increased tropical convection and increased upper level divergence in the tropics.

Consistent with the poleward movement of the jet streams, both the cyclone genesis regions and lysis regions move polewards. Interestingly, the median genesis region moves farther polewards (2 degrees) than the median lysis region (1.8 degrees). The number of extra-tropical cyclones decreases by 4.5% when the SSTs are warmed; in the control simulation there are 3496 cyclones but only 3338 in the warmed experiment (Table 1). However, when the distributions of maximum extra-tropical cyclone intensity are considered only small differences are observed to occur by warming the SSTs
by 4 K (Table 1). There is, however, a slight indication that there are more very intense extratropical cyclones in the warmer experiment and the maximum vorticity distribution is broader (larger standard deviation) than in the control simulation.

Figure 1: Cyclone composites 24 hours before the time of maximum intensity from control simulation (a,b) and the difference between the SST+4K experiment and the control (c,d). a and c show total column water vapour (kg m$^{-2}$). b and d show total precipitation (mm day$^{-1}$).

The cyclone composite of total column water vapour (TCWV, Figure 1a) and total precipitation (Figure 1b) 24 hours before the time of maximum intensity in the control simulation confirm that realistic cyclones are simulated. The highest TCWV values occur south and east of the cyclone center, in the warm sector and low values of TCWV are present to the north and west, indicative of dry descending air behind the cold front. The maximum precipitation occurs north and east of the cyclone center, essentially at the leading edge of the high TCWV values.

The cyclone composites also show that the structure of cyclones changes when the SSTs are warmed. Total column water vapour is larger everywhere in the cyclone composite from the SST+4K experiment (Figure 1c), compared to in the control simulation composite, as expected. However, the increase in total column water vapour is not spatially uniform; the largest increases occur to the south and east of the cyclone center and are greatest during the intensification phase of the cyclone. The spatial pattern of precipitation associated with extra-tropical cyclones also changes...
when the SSTs are warmed. In the region of the warm front, to the north-east of the cyclone center, precipitation increases whereas close to the surface cold front, precipitation decreases (Figure 1). These preliminary results indicate that, in the future, as our climate warms, that the structure of extra-tropical cyclones may change.

ACKNOWLEDGEMENTS

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SEASONAL VARIATION AND TIME SERIES OF AEROSOL OPTICAL DEPTH OVER DIFFERENT

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Keywords: AEROSOL, TIME SERIES, SATELLITE, CHINA.

INTRODUCTION

For several decades, China has been considered as a strong source of atmospheric pollution. Growing economy
and pollution regulation legislation, natural emissions (e.g., dust), long-range transport and meteorological
conditions are the main factors, which influence the aerosol seasonal distribution and long-term changes in
aerosol loading in China. Because of the strong variation in geographical conditions (Tibet Plateau in the south-
west, the Taklimakan desert in the north-west, the North China plain in the east, surrounded by mountains at the
west and north and the sea at the east and south), the population and industry, which are the main source for
emission of atmospheric pollutants, are not evenly distributed in China. Thus, differences in aerosol loading and
seasonal cycles are expected in different parts of China.

The aim of this study is to reveal the differences in aerosol conditions in different regions of China and follow
the changes in aerosol loading during the last two decades using the Aerosol Optical Depth (AOD) retrieved
from satellites using the (A)ATSR and MODIS instruments.

METHODS

ATSR Dual View (ADV) retrieval algorithm for aerosols (Kolmonen et al., 2016, Sogacheva et al., 2017) and
clouds have been developed for the (A)ATSR, consisting of a series of instruments: ATSR-2 which flew on the
ERS-2 satellite (1995-2003) and AATSR which flew on the ENVISAT satellite (2002-2012), both from the
European Space Agency (ESA). ADV AOD has been validated over China (Sogacheva et al., 2017), showing a
good (0.89) correlation with reference data from the ground-based sun photometer network AERONET (Holben
et al., 1998) with small underestimation of AOD in a range 0.5-1.

AOD from MODIS Terra C6, merged form the Dark Target and Deep Blue (DT&DB) algorithms (Levy et al.,
2013) has been used for comparison with the ADV AOD products. MODIS DT&DB AOD validation with
Chinese Sun Hazemeter Network (Zhang et al., 2016) show good (0.9) correlation in the Beijing area with some
overestimation of AOD (bias 0.05, slope 1.15).

MODIS Terra overpass is ca. 1h behind the AATSR overpass. Thus, the direct comparison of the AOD retrieved
with two instruments is possible, keeping in mind the slight increase of AOD in the morning related to the
radiation and emission daily cycles.
Seasonal AOD for 10 selected areas over China (Fig. 1) averaged for the period 2000-2011 have been calculated and compared for the AATSR ADV AOD and MODIS Terra DT&DB AOD. ADV (1995-2012, combined from ATSR-2 (1995-2002) and AATSR (2003-2012)) and MODIS (2000-2015) AOD time series have been analysed with linear and 5-degree polynomial regressions.

RESULTS

ADV and MODIS seasonally averaged AOD for the 10 selected areas over China (Fig. 1) have similar yearly cycles in corresponding areas (de Leeuw et al., 2017). Spring maxima in the south (which might be related to the monsoon season) and west of China becomes less pronounced towards north and east. Summer maxima in AOD are observed over the most polluted North China Plain (Area 1 in Figure 1). MODIS AOD over China is higher than ADV AOD (Fig. 1). Several explanations for that exist. First, MODIS potentially slightly overestimates AOD over China, as shown in de Leeuw et al. (2017). Second, anthropogenic emissions are accumulated in the atmosphere during the morning hours and secondary aerosols are growing with some delay. Third, MODIS has better coverage than AATSR, especially in winter.

Figure 1. Seasonal AOD cycles (circles, W - winter, blue, S - spring, purple, S - summer, green, F - fall, yellow) for ADV (red line) and MODIS (blue line) averaged for the period 2000-2011 for different areas over China (red numbers on the map and corresponding sub-plots).

AOD time series for ADV (1995-2012) and MODIS (2000-2015) are plotted as yearly averages in Figure 2 and to estimate trends, 5-degree polynomial and linear regressions have been fitted to the data. The 5-degree polynomial fit generally reproduces well the trends in AOD, which are similar for both ADV and MODIS (Figure 2). Both data sets show a peak in areas 1, 5 and 10 in the years 2003, 2006 and 2011.
Figure 2. ADV (purple) and MODIS (green) AOD time series approximated with 5th-degree polynomial.

$R^2$ is the coefficient of correlation. Dashed lines indicate the 95% confidence intervals.
Linear regression (results not shown here) does not always reproduce well the AOD trend. However, we can conclude that positive AOD trends for the AATSR and MODIS periods of measurements (1997-2011 and 2000-2015, only full years are included into analysis) exist in areas, affected by anthropogenic emissions (areas 1-7). ADV often shows stronger increase of AOD than MODIS. For the remote areas (8-10), the AOD trend is negligible (Table 1).

Table 1. ADV and MODIS AOD trends for the areas (1-10) as on Figure 1 and Figure 2.

<table>
<thead>
<tr>
<th>Area</th>
<th>ADV AOD trend/year</th>
<th>MODIS AOD trend/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.015</td>
<td>0.013</td>
</tr>
<tr>
<td>2</td>
<td>0.009</td>
<td>0.004</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>4</td>
<td>0.011</td>
<td>0.003</td>
</tr>
<tr>
<td>5</td>
<td>0.006</td>
<td>0.001</td>
</tr>
<tr>
<td>6</td>
<td>0.005</td>
<td>-0.004</td>
</tr>
<tr>
<td>7</td>
<td>0.010</td>
<td>0.004</td>
</tr>
<tr>
<td>8</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>9</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>10</td>
<td>0.000</td>
<td>0.003</td>
</tr>
</tbody>
</table>

The preliminary results shown here will be further analysed, together with anthropogenic emissions and meteorological conditions.

Method to combine AOD time series from two instruments (ATSR and MODIS), which together cover more than 20 years of AOD measurements has been developed. Method and its application over China will be introduced in Sogacheva et al. (2017, in preparation for ACP).

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AEROSOL-CLOUD INTERACTIONS IN LIQUID CLOUDS OBSERVED DURING BAECC CAMPAIGN

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Keywords: AEROSOL-CLOUD INTERACTIONS, BIOGENIC AEROSOLS, BOREAL FOREST.

INTRODUCTION

Biogenic secondary organic aerosols (BSOA) can grow to cloud condensation nuclei (CCN) sizes and participate in cloud processes. Biogenic Aerosols – Effects on Clouds and Climate (BAECC) campaign (Petäjä et al, 2016) that took place at the SMEAR II station in Hyytiälä, Finland, made possible the collection of data that can be utilized to study ACI in boreal forest domain. It combined set of active and passive remote sensing instruments such as cloud radars, lidars and radiometers with comprehensive aerosol measurements. Our study focuses on the ACI in warm single-layer non-precipitating clouds in the active BSOA formation zone. We study the effect of CCN concentrations on the cloud effective radius ($R_e$) changes inside the cloud at different dry air entrainment levels.

METHODS

Cloudnet target classification dataset used to select single-layer liquid non-precipitating clouds. Such clouds occurred during five months (April to early September) throughout the campaign time. We combine reflectivity measurements from W-band ARM Cloud Radar (WACR) and liquid water path (LWP) measured with microwave radiometer to retrieve vertical profile of $R_e$:

$$r_e(h) = \left(\frac{(v + 2)^3}{(v + 3)(v + 4)(v + 5)}\right)^{\frac{1}{5}} \times \left(\frac{\pi \rho_w \sum_{i=1}^{n} Z_i(h_i) \Delta h_i}{48LWP}\right)^{\frac{1}{5}} Z_i(h),$$

where $\rho_w$ is water density, $\Delta h$ is radar range gate length, $Z(h_i)$ is reflectivity factor at the $i$th gate. Methodology described in detail Sarna and Russchenberg (2016). We exclude from each profile measurements from the lowest gate inside the cloud and above the height where reflectivity reaches maximum values. This ensures that gates that are only partially filled with cloud and cloud tops that normally characterized by higher level of entrainment.

Dilution coefficient $k$ is defined as ratio of measured liquid water content (LWC) to the theoretical LWC. Measured LWC is estimated from modelled at the cloud base LWC which is scaled so that its integral matches radiometer measurement of LWP so that LWC follows quasi-adiabatic profile. If $k$ value equals 1, this means that clouds are adiabatic. Dilution coefficient values <1 indicate dry air entrainment processes. All suitable $R_e$ data are binned by dilution coefficient and surface-measured CCN concentrations; linear fit is performed for each of the bins.

RESULTS

Figure 1 shows an example of cloud that fulfils data selection criteria and allows retrieval of $R_e$. Theoretical predictions are that if such cloud is more polluted, available water would be distributed over greater number of cloud condensation nuclei. This would lead to higher concentration of cloud droplets
but of a smaller diameter. At the same time, dry air mixing processes cause evaporation of cloud droplets that also affects cloud droplet growth inside the cloud in a way that in more diluted clouds droplets would grow slower.

Figure 1. An example of a warm single-layer non-precipitating cloud occurred on 31st August and was selected for analysis: top) WACR reflectivity; bottom) Cloudnet target classification.

To study $R_e$ growth inside the cloud at different CCN concentration and dry air mixing levels, we binned all suitable data accordingly and calculated linear regressions which are shown on Figure 2. At lower CCN concentrations (0-100 cm$^{-3}$) in moderately diluted clouds (dilution coefficient $0.6 \leq k < 0.9$) cloud droplet size increases 2-4 times faster than at the CCN concentrations greater than 100 cm$^{-3}$. In less polluted clouds the effect of dilution is evident: in clouds close to being adiabatic, cloud droplets grow by 1µm every 10 meters inside the cloud while in strongly dilute clouds ($0.2 \leq k < 0.3$) this happens for every 30 meters. In clouds close to being adiabatic ($0.9 \leq k < 1.2$) the effect of CCN is not clear.

Figure 2. Cloud effective radius profiles at different CCN concentrations and dilution levels. Shown profiles are obtained with calculated linear regression over the binned data.
Very diluted clouds (0.0 ≤ k < 0.2) also do not exhibit such dependency which is expected considering that in decaying clouds it is unlikely to see strong effect of CCN on cloud droplet radius.

CONCLUSIONS

The results of this study provide evidence of interaction between BSOA and liquid single-layer warm clouds in boreal forest domain. The effect of dry air mixing on cloud effective radius and therefore radiative properties of the clouds is revealed. Applying the same data analysis methodology to more measurement sites and longer datasets would allow for improving the cloud properties parameterizations in models.

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REFERENCES

DO BIOTIC PLANT STRESSES INDUCE FORMATION AND GROWTH OF NEW PARTICLES?

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Keywords: VOLATILE ORGANIC COMPOUNDS, STRESS INDUCED EMISSION, AEROSOL FORMATION AND GROWTH, ATMOSPHERE-BIOSPHERE INTERACTIONS.

INTRODUCTION

Vegetation is the largest source of volatile organic compounds (VOCs) in the atmosphere (Guenther et al., 2012). Trees emit a variety of VOCs, but the source strength, chemical composition and structure of VOCs depend on the individual tree species, along with physical, environmental and biological conditions. VOCs are atmospherically and climatically important as they constitute secondary organic aerosol (SOA) precursor molecules and hence affect the formation and growth of new atmospheric aerosol particles that are capable of modifying climatically important cloud properties (Twomey, 1991; Charlson et al., 1992). Much attention has been given to representing the constitutive emissions (i.e. emissions as a by–product of plant metabolism) of VOCs in various modelling efforts. Unfortunately, VOC emissions caused by stress, and especially biotic stress, has been mostly excluded. As stress induced emission has been forecast to increase in frequency and severity in a warmer climate (Bale et al., 2002), the neglect of stress-dependent emission in climatic models could be one of the key obstacle for realistic climatic predictions.

METHODS

We constructed a model to study the impact of biotic plant stresses on new particle formation (NPF) and growth. The model includes atmospheric oxidation and the most recent advances in extremely low volatility organic compounds chemistry. Sulfuric acid and organic vapours participate in both the formation and condensational growth of new particles via non-equilibrium gas-particle partitioning. Published records on the emissions of VOCs from oak, poplar and birch due to herbivory and fungal infections are also implemented, alongside their constitutive VOC emissions. We considered pedunculate oak infected with oak powdery mildew or European gypsy moth, mountain birch infected with autumnal moth, and Populus balsamifera var. suaveolens infected with rust fungus. We chose to focus on these species, because oak is widely distributed in Europe, and it is one of the most economically important deciduous species in this region (Ducousso and Bordacs, 2004). Poplar and birch trees are common in most of the Northern Hemisphere and, especially in Europe, there is an increasing interest in growing poplars as a source of renewable energy (Directive 2009/28/EC; Benetka et. al., 2014), while birch is mostly used for plywood and furniture (Finnish Statistical Yearbook of Forestry, 2014). We considered these biotic stressors as the larvae have previously been reported to defoliate several thousands of square kilometres of forests (Tenow, 1975; Nikula, 1993), while the fungal infection level within an individual forest stand has been recorded to be at least 75% (Bert et. al., 2016). The tree species and biotic stressors that we studied are depicted in Fig. 1. We constrained the model with atmospheric observations from
the SMEAR I station (Station for Measuring Ecosystem – Atmosphere Relations), Väriö, Finnish Lapland, when simulating birch, since autumnal moth infection in mountain birch is most common in rocky Fennoscandia. Our model incorporated atmospheric conditions observed at the Meteorological Observatory Hohenpeissenberg when simulating oak and poplar stands, since this station is representative for central Europe, where these tree species are common.


**RESULTS and DISCUSSION**

We found that both constitutive and stressed VOC emissions from Fennoscandian mountain birch forests do not lead to NPF – independent on the severity of the stress. Sensitivity studies showed that a stressed mountain birch forest, in the conditions of Hohenpeissenberg, will form 2 nm particles (*J*₂ = 2.5 cm⁻³s⁻¹), but the particles will not grow to larger sizes due to lack of organic vapours.

A non-stressed oak stand only forms small particles (*J*₂ = 3.5 cm⁻³s⁻¹, *J*₅ = 0.16 cm⁻³s⁻¹), but these particles will not grow to larger sizes because of too small ELVOC concentrations. If the oak stand becomes infected by gypsy moth larvae, then up to ~70,000 particles/cm³ will be formed. For comparison, 10,000-20,000 new particles/cm³ is produced during a usual NPF event in Hyytiälä at the boreal SMEAR II station. Simulations show that if the oak stand was instead infected by
mildew, then only up to $\sim 1.800$ particles/cm$^3$ would be formed. However, our simulations show that in case of this fungal infection, the concentration ratio ($R$) of isoprene carbon to monoterpene carbon is at least $\sim 3.75$. Observations made in several forests indicate that NPF rarely takes place if $R > 1$ (see e.g. Lee et al. (2016)). This suggests that no NPF will be observed in a mildew infected oak forest.

Due to the very high constitutive isoprene emission from poplars, this tree species will not form new particles in non-stressed conditions. If the poplar stand becomes infected by rust, up to $\sim 18.000$ particles/cm$^3$ are formed. However, $R \geq 5$, hence it is questionable whether these particles are truly formed.

CONCLUSIONS

We constructed a model to simulate new particle formation and growth in various broadleaved forest stands under stressed and non-stressed conditions. Our results indicate that not all stresses lead to new particle formation, but that some do, and then the induction is tremendous. Since plants often experience some degree of stress, and since our study shows that individual stresses have highly different potentials to form new particles, it is crucial to measure the stressed emission caused by other mayor stressors.

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REFERENCES


UNSUPERVISED CLASSIFICATION OF VERTICAL PROFILES OF DUAL-POLARIZATION RADAR VARIABLES

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Keywords: SNOWFALL, WEATHER RADAR, VERTICAL PROFILE, GROWTH PROCESSES.

INTRODUCTION

The size, shape and degree of riming of a growing snow particle depend mainly on ambient temperature, supersaturation and presence of liquid water. As these ambient conditions are not constant through a vertical column, the significance of different growth processes vary along the paths of growing snow particles. Although, with remote sensing techniques we cannot directly measure which growth processes are taking place in a vertical column, dual polarization radar measurements of vertical columns can be viewed as containing fingerprints of these processes. Currently there are studies of individual features in the profiles, e.g. enhanced values of specific differential phase ($K_{dp}$) or differential reflectivity ($Z_{dr}$), but no attempts have been made so far to create objective documentation of such profiles.

METHODS

In the present study, an unsupervised classification method is applied for vertical profiles of dual polarization radar observations derived from RHI scans in southern Finland. The proposed classification method is based on k-means clustering of dimensionally reduced combination of vertical profiles of equivalent reflectivity factor ($Z_e$), $Z_{dr}$ and $K_{dp}$, and on ground temperature.

The aim of this study is to characterize different types of vertical profiles of dual polarization radar variables in winter precipitation and to link them to snowfall properties such as liquid water equivalent (LWE) precipitation intensity, ensemble mean density and degree of riming, as well as to other properties of the vertical column such as liquid water path (LWP). By employing the unsupervised classification method over the complete tropospheric profiles of polarimetric radar measurements we avoid making priori assumptions on the features of the snow process fingerprints these profiles contain. Instead we try to characterize the variety of observed profiles.

In this investigation we look at vertical profiles over Hyytiälä forestry station in Juupajoki, Finland using Ikaalinen weather radar which is located 64 km west from the station. Measurements have been performed during the Biogenic Aerosols – Effects on Clouds and Climate field campaign in early 2014, and the winter of 2014/2015. The training material for the classification currently consists of 15 snow cases, generally with full temporal extent of the event including profiles in which falling particles have not reached the ground.

CONCLUSIONS

With the proposed method we obtain a classification scheme of 19 separate classes, which explain roughly 90% of the observed variance in the profiles. In Figure 1, the class centroids are compared againsts LWE precipitation rate. As we are looking at temporal evolution of events, a large number of classes represent situations with precipitation rates close to zero. In 6 out of the 19 classes, the LWE precipitation intensity reaches at least 2 mm h⁻¹. The connection between high vertical extent of reflectivity profiles and high
precipitation rate is found to be strong. The profiles of high precipitation intensity also generally show a clear $K_{dp}$ signal, namely in classes 9, 11, 12 and 17. Among situations with high precipitation intensity, the lowest LWP values were connected with low temperature and vice versa.

Figure 1. The 19 cluster centroids of the vertical profile classification scheme as obtained by K-means clustering (top 4 panels) compared against liquid water equivalent snowfall rate (bottom panel).

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VOLATILITY OF α-PINENE DERIVED SOA WITH AND WITHOUT DECOMPOSITION OF DIMERS: WHAT CAN WE LEARN FROM THE EVAPOGRAMS?

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Keywords: α-PINENE, SOA, VOLATILITY, DIMERS

INTRODUCTION

Secondary organic aerosol (SOA) is formed when volatile organic compounds (VOCs) in the gaseous phase are oxidised to lower volatility compounds which can partition into the particle phase (Hallquist et al., 2009). The SOA consists of thousands of individual compounds (Goldstein and Galbally, 2007) many of which have not been yet characterized. Since a large fraction of atmospheric aerosols is SOA, this gap of knowledge hinders our understanding of the aerosol-cloud-climate interactions.

In many laboratory studies α-pinene has been used as a model compound for biogenic VOCs. Thus, the SOA produced from oxidation of α-pinene is thought to model the atmospheric biogenic SOA. There exists numerous studies on the properties of α-pinene derived SOA. However, due to the complex nature of the oxidation reactions and formation of the organic particles many properties of the SOA are still poorly understood. For example, volatility parametrizations derived from the growth experiments of α-pinene SOA (Pathak et al., 2007) has been shown to produce too fast evaporation when the same parametrization is used to model evaporation experiments (Vaden et al., 2011; Yli-Juuti et al., 2017).

Yli-Juuti et al. (2017) measured the evaporation of SOA derived from the ozonolysis of α-pinene at different humidities and concluded that effort should be put on capturing the volatility of the SOA particles with precision. Further, in their measurements the oxygen-to-carbon ratio (O:C) was relatively low and stayed constant during the evaporation, suggesting that the low volatility compounds might have been dimers, that have the oxygen-to-carbon (O:C) ratio comparable to the monomers that have higher volatility.

In this work we studied the evaporation of α-pinene SOA produced with a Potential Aerosol Mass reactor (Kang et al., 2007; Lambe et al., 2011) at high RH with the same evaporation chamber as Yli-Juuti et al. (2017). Using an evaporation model we sought to find the optimal volatility distribution at the start of the evaporation with which the measured evaporation can be described. Since the mass spectrometer data in our experiments showed that the O:C ratio was relatively low and did not change remarkably during the evaporation, we included the effect of dimer decomposition due to water interactions to our evaporation model to see how this affects the volatility distribution from the model.

METHODS

The SOA was created from photo-oxidation of α-pinene in a Potential Aerosol Mass (PAM) reactor. A monodisperse particle population was selected with a differential mobility analyzer (DMA) and led to a
stainless steel chamber with a volume of 100 L. The electrical mobility diameter of the particles was 80 nm. The chamber was filled for 20 minutes after which the chamber was closed and the outlet was opened later only for the determination of the particle size distribution with a scanning mobility particle sizer (SMPS). The RH during the experiment studied here was 78% and the length of the measurement over 8 hours.

To obtain data from the very first seconds of the evaporation, the size distribution of the evaporating particles were measured from a bypass of the chamber. In this case the particles were led directly from the DMA to the SMPS with copper tubing of various lengths. This way we were able to obtain data between 4 seconds and 1.5 minutes from the point where particles started to evaporate.

Besides particle size distribution measurements, the chemical composition of the particles was measured with High Resolution Time-of-flight Aerosol Mass Spectrometer (HR-ToF-AMS).

The measured evapograms (particle diameter relative to the diameter at the start of the evaporation as a function of time) were interpreted assuming that at the high RH of the experiments the particles behave like well-mixed, liquid-like particles i.e. there are no diffusional limitations in the particle phase and that the gas phase inside the chamber had infinite dilution. We considered two possible scenarios for the evaporation at this high RH. In both cases the volatility of the particles was described with a volatility basis set approach (VBS, Donahue et al., 2006). In the first scenario we considered that the size change of the particles is due to the evaporation of non-interacting compounds. In the second scenario we included the decomposition of long-chained molecules that can break due to the interactions with water producing two molecules with a higher volatility. This effect was modelled by labeling a fraction \( F_{\text{dimer}} \) of the least volatile species as dimers that decompose with a constant rate of decomposition \( k_{\text{decomp}} \).

Based on the above scenarios we developed two evaporation models which calculate the particle size change as a function of time. As input the models require the physicochemical parameters of the evaporating species and their relative amount in the particle phase at the start of the evaporation. We optimized the initial composition of the particles by minimizing the squared distance between the measured points and the simulated evaporation curve. For the optimization algorithm we used a Monte Carlo Genetic Algorithm (MCGA, Berkemeier et al., 2017). For the other parameters besides saturation concentration, a same molar mass \( (M=200 \text{ g/mol}) \), density \( (\rho = 1.2 \text{ g/cm}^3) \) and gas phase diffusion coefficient \( (D_g = 0.05 \text{ cm}^2/\text{s}) \) were assumed across all the evaporating organic species. The only difference to these assumptions was the molar mass of dimers which was set to \( M=400 \text{ g/mol} \) in order to conserve the mass during the decomposition.

RESULTS

Figure 1a shows the preliminary results where the initial composition of the particle is optimized with and without the decomposition effect of the dimers. In these simulations the particle consisted only of three evaporating species with C* of \( 10^{-3} \mu \text{g/m}^3 \), \( 10^0 \mu \text{g/m}^3 \) and \( 10^2 \mu \text{g/m}^3 \). The volatility distributions resulting from five independent simulations are shown in figures 1b and 1c. In figure 1c the y-axis also shows the fraction of the least volatile bin that is labelled as dimers \( F_{\text{dimer}} \) which decomposes to the second most volatile bin. Not shown in the figure 1c is the decomposition rate \( k_{\text{decomp}} \) which varied between ca. \( 10^{-5} \) and \( 10^{-4} \text{ s}^{-1} \) in the five independent simulation.

The start of the evaporation can be captured well with three evaporating species and without the decomposition effect (blue line in figure 1a). The model fails to capture the size change especially between 10 and 130 minutes when the modelled evaporation is too fast compared to the measurement one. Further, the model in this first scenario seems to indicate that after 50 minutes the particles consists solely of the least volatile species producing negligible evaporation compared to the measurements.
The initial particle composition in the simulations without the decomposition effect shows that 56% of the molecules need to be in the least volatile bin, 34% in the second most volatile bin and 10% in the most volatile bin. It is to be noted that the MCGA algorithm produces nearly the same particle composition for five different simulations. This means that with three evaporating compounds the model is sensitive to the mole fractions of each compounds at the start of the evaporation and that with three species there is likely no better initial composition that would produce better fit to the measurements than the one found here.

Optimizing the particle composition with the model that includes the dimer decomposition produces better fit to the measurements (black dashed line). The squared sum of residuals between the evaporation curve and the measurements is at best over half a magnitude lower than in the case of no dimer decomposition. However, adding the two extra parameters (\(F_{\text{dimer}}\) and \(k_{\text{decomp}}\)) leads to variation in the mole fractions. In this case to be able to capture the measured particle size change 49-57% of the dry particle molecules need to be in the least volatile bin, 19-29% in the second most volatile bin and around 10-15% in the most volatile bin. The fraction of dimers varied between 21-46% of the least volatile bin and the decomposition rate of the dimers between \(10^{-5}\) and \(10^{-4}\) s\(^{-1}\).

**CONCLUSIONS**

We modelled the evaporation with two different single particle models based on the VBS approach: One where the evaporation is dependent only on the saturation concentrations and amounts in the particle phase of non-interacting compounds and the other where a fraction of the least volatile compound is labelled as dimers which can decompose to the second most volatile bin.
The relatively low and constant O:C of 0.53 in our measurements does indeed hint that the O:C ratio between different compounds is similar and that the low volatile particle phase compounds are dimers which have O:C ratios similar to their monomers instead of highly oxidized compounds. Assuming that these dimers decompose from interaction with water does lead to a better agreement with the model and the measurements. It is to be noted, however, that the same behaviour can be modelled also by adding more semi-volatile species to the model. Adding additional evaporating compounds increases the variance in the initial amounts of each species in the particle at the start of the evaporation and hinders our analysis on the effect of dimer decomposition to the model results. To be able to constrain the role of the dimer decomposition in the produced SOA better, measurements spanning to length scale of days would be needed.

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IMPROVING THE REPRESENTATION OF MIXED-PHASE CLOUD MICROPHYSICS IN THE ICON-LEM

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Keywords: cloud microphysics, mixed-phase clouds, cloud-resolving model

INTRODUCTION

Clouds are of critical importance for the Earth's radiation budget and the hydrological cycle. Therefore understanding the physics of clouds in changing ambient conditions, both due to greenhouse gas induced warming and anthropogenic aerosol emissions, is essential in order to understand the climate change.

This calls for accurate methods to represent cloud microphysical properties in numerical models in both liquid and ice clouds. For this, two-moment microphysical schemes, which predict the number and mass of cloud droplets and ice crystals, are the most widely used tools. However, modelling the properties of ice clouds has proven to be a particularly challenging task. One significant source for uncertainties in modelling ice clouds arise from the techniques used to describe the properties of the several different types of ice particles, such as cloud ice crystals and the rimed ice species such as graupel and hail, which have quite different physical characteristics. To account for this, cloud microphysical schemes most often divide the ice particles into predefined categories, imposing fixed assumptions for the physical properties of the particles. In this work, we improve the representation of the cloud microphysical properties in the ICOsahedral Non-hydrostatic Large-Eddy Model (ICON-LEM; Dipankar et al., 2015) by implementing a new cloud microphysical scheme with novel methods for describing the range of ice particle physical properties.

METHODS

We will make use of the recently published Predicted Particle Properties (P3) scheme (Morrison and Milbrandt, 2015). Figure 1 shows a schematic of the differences between a typical two-moment microphysical scheme (such as Seifert and Beheng, 2006; “SB” from now on) and the P3. Instead of using the fixed categories for different ice particle types, the P3 uses only a single category, but adds new prognostic equations for the mass and and volume mixing ratios of rimed ice, in addition to the usual set of prognostic equations for the number and total mass mixing ratios of ice. The advantages of this approach are that with the help of the new equations, the scheme can smoothly describe the range of variation in the particle properties, such as density, which affects e.g. the sedimentation of the ice particles. In addition, this approach avoids making uncertain assumptions about the transitions of particles between the different categories, which would otherwise arise, because the typical two-moment approach does not give adequate information to robustly determine the category where a particle should be allocated.
The P3 is implemented to the ICON model, which is used in the Large-Eddy Model configuration, i.e. subgrid turbulence is described according to the Smagorinsky-Lilly approach. Test runs are performed based on the idealized setup for deep convection given in Weisman and Klemp (1982), which is initialized using a warm bubble near the surface at the center of the domain. The model is run with a horizontal resolution of approximately 600 m. The vertical resolution is set as 20 m near the surface, and stretched to 100 m higher up in the atmosphere. The model top is at 21 km. In addition to the idealized simulations, a 1-day real-case experiment is performed for additional testing, with the lateral boundary conditions taken from the COSMO-DE analysis fields. The performance of the P3 is compared with experiments using the SB scheme, which is the default choice in the ICON-LEM.

CONCLUSIONS

In the idealized convection, the implementation of P3 causes quite significant differences in the timing of the precipitation onset and the strength of the convection. Especially the latter is mostly related to the different approaches for condensation of water vapour on cloud droplets in the SB and P3 schemes: while SB relies on saturation adjustment, P3 solves explicit condensation equations. This most likely causes the strength of the convective core updrafts to be overestimated in the simulations with SB due to too strong latent heat release.

Even though the bulk of macroscopic cloud properties show much similarities between the two microphysical schemes (for the primary convective updraft before the dynamical pathways of the storm diverge due to microphysical effects), the P3 microphysics yields clear differences in the cloud ice microphysical properties. For example, the rime fraction is somewhat higher than in the runs with the SB scheme, for which an explanation can be directly derived from the different assumptions between the two schemes. Moreover, the discretization of particles to fixed categories in the SB scheme yields somewhat different vertical distribution of the ice mass, especially for rimed ice species, as compared to the results with the P3 scheme.

A brief analysis of the real-case simulations are performed for further comparison. The results are compared with ground and satellite-based remote sensing observations. These results indicate that the P3 yields comparable results with the SB scheme, with somewhat improved results regarding the cloud ice water path.
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REFERENCES


UTILIZING OPEN ENSEMBLE PREDICTION SYSTEM ESTIMATING PARAMETER VALUES OF OPENIFS

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Keywords: ensemble forecasting, parameter estimation

INTRODUCTION

Ensemble weather forecasts are run operationally in national and international meteorological organizations around the globe, and the products are nowadays used to supplement the traditional deterministic weather forecasts. Ensemble forecast can also be utilized for various research purposes, for example estimate values of model closure parameters (Ollinaho et al. 2014). So far a major problem has been that there are no ensemble prediction systems (EPS) easily available for the academia. Moreover, EPSs used in operational forecasting centers are often rather stiff, difficult to use and tied to specific super computer system.

The Open Ensemble Prediction System (OpenEPS) is a framework for running model ensembles, and designed for research use. It is meant to be flexible and non system specific so that it could be installed on any machine.

The purpose of this study is to test OpenEPS and show that it is a feasible tool for non-operational ensemble forecasting for research purposes. This study also shows that OpenEPS is a versatile platform for applications. As an example application we implemented the ensemble prediction and parameter estimation system (EPPES) developed by Laine et al. 2012. EPPES is designed for estimation of parameters in numerical weather prediction (NWP) models (Järvinen et al. 2012, Laine et al. 2012).

METHODS

For this study, OpenEPS will be used to run ensembles of Open Integrated Forecasting System (OpenIFS) of European Centre for Medium-Range Weather Forecasts (ECMWF) as it is the most familiar model to the authors. OpenIFS is plain forecast model used in operational weather forecasting at ECMWF. OpenIFS does not contain data assimilation, and therefore it requires externally generated initial conditions. In the testing of OpenEPS we used a very low resolution version of OpenIFS to simplify and speed up the tests. The resolution was T21 that corresponds to about 1000 km horizontal grid spacing corresponding to a crude, but realistic, presentation of the atmospheric processes. The output fields of the model can be used as input for calculation of cost function value.

OpenEPS was run both on laptop and on Taito super cluster off line and on line. This was beneficial as small scale testing was still possible when Taito was out of use.

The tests we conducted with OpenEPS were basic convergence tests with two parameters and ensemble forecasts of different sizes. The convergence tests work so that EPPES tries to find the default parameter value used in the control forecasts by comparing ensemble forecasts to control forecasts acting as artificial truth. Initially wrong parameter values and large uncertainties are given for EPPES. In order to simplify the problem even more, the ensembles were run from a single initial state. Length of the individual forecasts were 24 hours.

Parameter estimation requires calculation of cost function between the ensemble members and the control forecasts. The cost function was calculated using the discretized dry total energy norm used by eg.
Ollinaho et al. (2014). We are particularly interested in small ensembles as they are cheap to run. Comparison of small and large ensembles enabled us to test our hypothesis that convergence is independent of ensemble size. The parameters we chose were ENTSHALP and ENTRORG. ENTSHALP is entrainment\(^1\) rate for shallow convection and ENTRORG is entrainment rate for deep organized convection. In the convergence tests we gave slightly altered initial mean values and large initial uncertainties of ENTSHALP and ENTRORG for EPPES. EPPES uses information about the mean values and the uncertainties and suggests normally distributed parameter values for the ensemble members. The ensemble members with parameter values close to the values in the control forecast should perform better so EPPES should give significant portion of resampling weight for them and they should steer the parameter values towards the default values. Eventually the parameter values estimated by EPPES should converge towards the default values in the control forecast.

**RESULTS**

The results show that ENTRORG converges towards the default value 0.00175 used in the control forecasts (figure 1 a, b). Moreover figure 1 shows that size of the ensemble forecasts does not affect the convergence significantly. However, the convergence may be less smooth at the beginning with small ensembles because it is difficult to adjust EPPES working so that one ensemble member would not solely affect the resampling process and parameter estimation would still be efficient at the same time. The hypothesis is correct with this parameter. Convergence is so good because the cost function has a strong global minimum and almost no local minima (not shown).

Figure 1. Convergence of ENTRORG (= entrainment rate for deep organized convection) with ensemble size 3 (panel a) and with ensemble size 20 (panel b). X-axes show the number of ensemble forecasts and y-axes show parameter values. The red curves are the parameter mean values given by EPPES, the blue curves are the mean \(\pm\) two times the standard deviation and the green lines represent the default value 0.00175 used in the control forecasts. The estimation process begins from value 0.0025. Dots represent parameter values in individual ensemble members. The darker the dot, the smaller the cost function value and more the member has got weight in resampling. EPPES updates the parameter mean values and uncertainties according to the dark dots. Numbers on the right show the final parameter mean value and \(\pm\) 2 standard deviations.

On the other hand, ENTSHALP does not converge well especially with small ensemble size (figure 2 a). Convergence is slightly better with larger ensemble size (figure 2 b). This is result is in contradiction with the hypothesis. We think that this problem of poor convergence is caused by the cost function used in the parameter estimation. Dry total energy norm may not be optimal cost function to measure the difference between the forecast and the “truth” in this case. Variation of ENTSHALP causes variation in moisture content of lower troposphere whereas dry total energy norm does not account for differences in moisture content. Differences in the moisture content will eventually affect dry dynamics of the atmosphere in a way or another so dry total energy norm will eventually see differences. However, EPPES cannot determine the connection between parameter variations and value of the cost function. Therefore the shape of the cost function is flat and it contains numerous local minima and the global minimum is very narrow (not shown). Dry total energy norm is not suitable cost function for estimation of ENTSHALP. However, switching on stochastic physics in OpenIFS improves the convergence to some extent (not

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1 Entrainment means turbulent mixing of air into convection from outside the convection.
shown). This could indicate that stochastic physics smooths the cost function so finding the global minimum becomes easier.

**Figure 2.** As in figure 1 but for ENTSHALP (= entrainment rate for shallow convection). Default value in the control forecasts is 2.0. The estimation process begins from 2.5.

**CONCLUSIONS**

OpenEPS is working well and is now ready for implementation of new applications besides EPPES. Also parameter estimation with EPPES works although the cost function used is not suitable for all parameters. Adding more criteria into the cost function could improve the convergence of ENTSHALP parameter. Another option would be a parameter estimation algorithm that accepts multiple cost functions.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


THE VERTICAL VARIATION OF SCOTS PINE STEM MONOTERPENE AND METHANOL EMISSIONS

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Keywords: VOLATILES, TERPENES, WOODY COMPARTMENTS, PINUS SYLVESTRIS.

INTRODUCTION

The woody compartments of living trees have been an unstudied and often also underrated as a source of biogenic volatile organic compound (BVOC) emissions. However, many tree stems especially in the boreal zone possess substantial storages of secondary metabolites and rely in resin-based defences (Phillips & Croteau 1999). The most prominent substrate is coniferous resin, a mixture of volatile mono- and sesquiterpenes and non-volatile resin acids. Scots pine (Pinus sylvestris L.), the most abundant tree species in Finnish forests, has an extensive resin duct network in its stem, with vertical and horizontal canals connecting different tree parts.

Pine bark is a good protection against external damages and internal loss of water vapour. However, several VOCs escape through the bark and its pores. Bark thickness varies between different tree parts being thickest at the tree base. In the data of Wilhelmsson et al. (2002), bark thickness of 527 pines varied between 1.5 and 23 mm. Not only bark thickness varies, but also its properties. Thin bark in the young parts is greenish and sensitive to damages, whereas the old and grey bark is much tougher. Moreover, young bark is usually constantly thin, while old bark has thick and thin spots because of cracks.

As mentioned above, pine bark allows some volatile compounds to escape to the ambient atmosphere. Methanol, the simplest alcohol, is rich in the lower atmosphere, and it is abundant also in plant emissions. In plant tissues, it is produced by the demethylation of pectin during cell wall expansion (Fall & Benson 1996). Globally, plant growth accounts for two thirds of the annual methanol emissions (Galbally & Kirstine 2002). In mature and non-growing plants, methanol emission may be related to the maintenance: cell wall components are in continual turnover to maintain their plasticity (Folkers et al., 2008). Other methanol sources include e.g. biomass decay and burning (Galbally & Kirstine 2002).

Until recently there has been almost total lack of information of the BVOC emissions from woody parts of living trees. Here, we offer a look into the vertical variation of emissions: do emission rates and blends vary along the stem, and if so, how? Here we concentrate on monoterpenes and methanol, which both show measurable emissions from Scots pine stems in situ.

METHODS

The BVOC measurements were carried out at the SMEAR II -station (Station for Measuring Ecosystem-Atmosphere Relations), Juupajoki, Finland, in a Scots pine stand. The emission rates of selected compounds were measured in field conditions using an automated gas-exchange measurement system coupled with a proton transfer reaction-quadrupole mass spectrometer (PTR-Q-MS, Ionicon Analytik GmbH, Innsbruck, Austria). There were three stem enclosures at different heights of a pine stem: the lowest one was at 7 m below the canopy. Another enclosure was situated inside the living canopy at the
height of 12 m. The third one was close to the treetop at 16.5 m, where stem diameter was only 3.5 cm. The chambers enclosed a part of stem similarly as in Vanhatalo et al. (2015).

To study qualitative differences in terpene emissions, the air in the above-described enclosures was sampled on adsorbent tubes filled with Tenax TA and Carbopack B. This was done occasionally in different seasons between 2012–2015. The adsorbed compounds of the sample tubes were analysed with a thermodesorption-gas chromatograph-mass spectrometer (TD-GC-MS).

RESULTS AND CONCLUSIONS

The results show an emission rate gradient along pine stem: the treetop emits more than the lower stem, presented per stem bark area. Partly this is caused by environmental conditions and partly by the internal tree physiology: Treetop is exposed to the full irradiation for the most part of a day unlike the lower stem, which stays cooler as canopies shade it almost entirely. Higher temperatures lead to higher biological activity and higher volatility of synthesized secondary metabolites. On the other hand, lower tree stem is older and less active, which is reflected also in the volatile emissions.

Figure 1 presents an example of the time series of stem monoterpene and methanol emissions. In the beginning of April, there was still snow covering the ground and the trees had not started their growth yet. Thus, the observed methanol flux visible does not originate from dividing plant tissues.

![Figure 1. Monoterpene (a) and methanol (b) emission rates at different heights of Scots pine stem in early spring 2013. The panel b includes only the times, when relative humidity in the enclosure has been below 70%. At that time of the year, sunshine hits the treetop, but only seldom reaches the lower parts of stem, which partly explains the lower emission rates. Dots represent the individual measurements and dashed lines the three-hour averages.](image)

The low number (n = 31) of the adsorbent samples do not allow far-reaching conclusions about the qualitative vertical variation of the monoterpene emissions. The results, however, show plenty of
qualitative variation (Fig. 2). The monoterpene emission bouquets and emission strengths varied a lot even in the consecutive days without any notable stress factors that could explain the changes (data not shown). In the literature, the monoterpene pool in stem resin reservoirs has been thought to be stable in non-stressed conditions, mainly due to its substantial size. Our compound-specific data on monoterpene emissions disagrees with that view.

Figure 2. An example of the vertical variation of monoterpene emission blend. The adsorbent tube samples were collected from the stem enclosures of the same pine on 23rd–24th July 2013.

The monoterpenes observed likely originate from that section of the stem, which was enclosed, though Trapp and Croteau (2001) have claimed that resin may flow several meters within a conifer resin duct network. It is hard to see that resin would remarkably move within an undamaged stem in conditions, where it is continuously rather amorphous and stem temperature is continuously rather low. The transport of methanol is, on the contrary, very likely to occur within a tree, as methanol is a water-soluble compound and may move easily in stem sap flow between roots and canopy. According to Sander (2015) and the references therein, the Henry’s law constant for methanol as gas and water as solvent is $3.6 \times 10^{-2} - 2.8 \text{ mol m}^{-3} \text{ Pa}^{-1}$. In the case of monoterpenes, Henry’s law constants are compound-specific, but for example $\alpha$-pinene has the constant of $7.4 \times 10^{-5} - 2.9 \times 10^{-4}$ (Sander, 2015). This is much lower than the ones for methanol, which tells about the lower solubility and thus the ability to move within tree tissues.

As a sum-up, the upper part of stem dominates the monoterpene emissions from Scots pine stem. Considering that the foliage is located in the uppermost part of tree as well, it is reasonable to say that the clear majority of Scots pine monoterpene emissions are released into the ambient forest air at the canopy heights. This information may have implications for the atmospheric chemistry modelling of below- and within-canopy air.

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REFERENCES


We have participated in several acts of writings, public discourses and seminars concerning the effects of forest utilization on climate and biodiversity (e.g. Seppälä et al, 2015; SITRA 2016; EURACTIV 2017; EASAC 2017; BIOS, 2017; Seppälä et al, 2017; Vesala and Kotiaho, 2017; Hukkinen et al, 2017). Writings include, among other things, long reports (multiple authors), newspaper columns and public letters (multiple authors). Finland is planning to increase substantially harvesting of timber, which leads, in the short-term (by mid 2000 century), increased carbon dioxide emissions into the atmosphere. Based on best available scientific understanding, these communications and writings have criticized the plans, which eventually lead to situation where the forest management actions in Finland are against the targets set by the Paris Climate Agreement and endanger the present level of biodiversity.

The core of the criticism has been in the planned massive intensification of forest use as bioenergy, leading to increased harvests in the expense of carbon storage and sinks, and possibly even harvesting previously economically non-profitable stands with the help of government subsidies. This view has been based on the proposed carbon neutrality of forest biomass, however it is not accounting for e.g. the poor energy content of forest biomass in comparison to other energy sources, nor the climate relevant emissions from forest harvesting which last for decades after clear-cut. Therefore, the climate neutrality of forest-based bioenergy can be questioned.

The comments and feedback we have obtained have varied greatly, depending on the perspective of the commenting persons and organisations. The discussion fora for replies have ranged from social media to newspaper articles and policy debates in scientific arena. On the one hand, we have been acknowledged for participating in the important socio-economic debate, for bringing the scientific arguments to the discussion and for clarifying the complex problem, where the terms and concepts are sometimes presented very vaguely. On the other hand, we have been accused for, e.g., being extremely narrow-minded and biased, for forgetting the economic realities and being unpatriotic, in addition to presenting dangerous things towards Finland and the finnish pulp and paper industry. Our statements are blamed to be post-truth politics and representing green left values without scientific facts.

In this presentation we aim at clarifying the background of this public dialogue and argue that a scientists’ responsibility is to participate also in public debates that concern the research field (s)he is working with. The Center of Excellence in Atmospheric Sciences is in a position where we are able to provide strong scientific argumentation on the climate change questions, and thus effectively contribute to the policy-relevant dialogue.

REFERENCES


NOVEL ASSESSMENT OF BLACK CARBON IN THE EURASIAN ARCTIC (NABCEA)

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Keywords: Black carbon, Flaring, Ice cores, Scenarios

INTRODUCTION

Black carbon (BC) is estimated to be the second most important climate warming pollutant after CO\textsubscript{2}. The recently started 4-year project Novel Assessment of Black Carbon in the Eurasian Arctic: From Historical Concentrations and Sources to Future Climate Impacts (NABCEA), 1 September 2016 – 31 August 2020, funded by the Academy of Finland, will produce new research knowledge on BC emitted from increased economic activity in the Arctic, especially flaring associated with oil and gas drilling, shipping, and domestic heating by small-scale wood combustion. These are increasing emission sources but their effects on Arctic climate change are not well known. The objective of NABCEA is to identify the most important BC sources affecting the warming and melting in the Arctic in the recent past, present and the future. The detailed goals of the project are 1) to quantify the contribution of the most important sources, especially flaring related to oil drilling, shipping, and wood combustion to the BC observed in the Arctic atmosphere, snow and ice in the present time and in the recent past, 2) to quantify the climate forcing of BC in the atmosphere and snow, and 3) to estimate how the above-mentioned processes/impacts affect Arctic climate during the next 50 years.

METHODS

The project consists of field and laboratory experiments, analyses of existing field samples, and modeling. The five work packages (WP1 – WP5) of the project are depicted schematically in Figure 1.

In WP1, BC analyses will be made for ice core samples collected from glaciers in Svalbard, and lake sediment samples from north western Russia (flaring area), Finnish Lapland, and Svalbard to determine past BC concentrations and deposition in the Arctic. These data will help in the assessment of past and modeling of future climate impacts of BC pollution in the Arctic. The relative contribution of contemporary biomass versus fossil fuel combustion to the BC in the samples will be determined by radiocarbon measurements.
An important goal is to decipher whether the increase in BC concentrations (Figure 2a) observed in 1970-2004 in the Holtedahlfonna ice core (Ruppel et al., 2014) has continued, and whether it is a local signal or can be found in other glaciers and/or lake sediments as well.

Figure 2. BC concentrations observed in an ice core a) in Svalbard and b) in Greenland (McConnell et al., 2007). The figure is adapted from Ruppel et al. (2014).
In WP 2, the present BC concentrations in air and snow are determined from ground-based measurements at the Pallas-Sodankylä GAW station in Finnish Lapland, and at Tiksi, Yakutsk, in the Russian Siberia in cooperation with the Russian Roshydromet and the US NOAA. New measurements have been started on the Bolshevik island at Cape Baranova station in collaboration between the Russian Arctic and Antarctic Research Institute (AARI) and FMI. Snow samples have already been and will be collected from several sites in the Arctic: northern Scandinavia, Svalbard, and sites in northern Siberia. Samples will be taken in a gradient from near the sources (Yamal Peninsula, in respect of flaring) to the background (Tiksi (Siberia), Svalbard).

In WP 3, the evolution of physical properties and chemical composition of BC aerosols emitted from burning processes will be studied in laboratory experiments at the University of Eastern Finland (UEF). Two experimental campaigns, one for flaring emissions and another for wood combustion emissions will be performed during the project.

In WP 4, Finnish Environment Institute (SYKE), in collaboration with the International Institute for Applied Systems Analysis (IIASA), will study the emissions and the resulting concentrations of BC in air and snow in the current and future Arctic. The scenarios will be done by using the Greenhouse Gas and Air Pollution Interactions and Synergies model (GAINS, gains.iiasa.ac.at). Special attention from the Arctic perspective will be paid to the emission sectors prioritized in this project.

In WP 5, the current and future BC radiative forcing in an Arctic-wide scale will be estimated by using the NorESM climate model, which has a relatively sophisticated treatment of snow and aerosols. Emission scenarios developed in WP4 will be employed. This task will be supported by off-line radiation calculations and comparison of NorESM results with in situ observations collected in the projected.

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LOWER TROPOSPHERIC WARM ANOMALIES OBSERVED AFTER PRECIPITATION OVER TROPICAL OCEANS

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Keywords: DEEP CONVECTION, HUMIDITY, PRECIPITATION, SOUNDINGS.

INTRODUCTION

Atmospheric deep convection produces most of the precipitation on Earth, and it is the main mechanism for the vertical transport of water vapor in the atmosphere. Since water vapor is one of the most important greenhouse gases on Earth, depicting accurately the behaviour and effects of deep convection in climate models is crucial. As deep convection results in heavy rain showers and is the main mechanism behind many severe weather phenomena, such as thunderstorms, hurricanes and tornades, its physics should be understood and parameterized accurately also in numerical weather prediction models.

One of the fundamental constraints on deep convection is sufficient amount of lower tropospheric moisture (e.g. Brown and Zhang, 1997; Bretherton et al., 2004). Although this relationship has been studied extensively, the basic mechanism for the relationship is yet to be completely understood. The sensitivity of deep convection to lower tropospheric moisture is often explained to be due to entrainment of environmental air into cloud updrafts (e.g. Holloway and Neelin, 2009). Here we present an observational analysis of sounding and precipitation data and propose another mechanism to explain, in addition to entrainment, the sensitivity of deep convection to the amount of moisture in the lower troposphere.

METHODS

We have utilised sounding data from the Integrated Radiosonde Archive and daily precipitation data from the Tropical Rainfall Measuring Mission. The time period of investigation was November-February 1998-2014 and the data was selected from eight sounding stations, of which seven were located in the tropical Western Pacific and one over the Eastern Indian Ocean. Each sounding at each station was classified to a group based on the amount of 5°x5° area-averaged precipitation obtained during the 24 hours just before the sounding. Six precipitation groups were formed so that the precipitation thresholds for the groups were: < 0.5 mm day⁻¹ in PRG0, 0.5-1 mm day⁻¹ in PRG1, 1-2 mm day⁻¹ in PRG2, 2-5 mm day⁻¹ in PRG3, 5-10 mm day⁻¹ in PRG4 and > 10 mm day⁻¹ in PRG5. From hereon, PRG0 group is called the “non-precipitating group” and the rest of the groups (PRG1-PRG5) “precipitating groups”. A mean vertical profile of temperature for each precipitation group at every station was calculated. For every station, a vertical temperature profile that is called the “piecewise mean” was also calculated. The piecewise mean vertical profile of temperature for each station was constructed by calculating the average of the mean vertical temperature profiles in the six precipitation groups (PRG0-PRG5). The piecewise mean was subtracted from the mean vertical temperature profiles in each precipitation group because in the tropics it is more convenient to study vertical profiles of temperature differences rather than of absolute temperature. From hereon, we define that a “warm anomaly” has occurred if temperatures in the precipitating groups (PRG1-PRG5) are warmer than in the non-precipitating group (PRG0), and that a
“cold anomaly” has occurred if temperatures in the precipitating groups (PRG1-PRG5) are colder than in the non-precipitating group (PRG0).

CONCLUSIONS

The vertical profiles of temperature differences revealed that after precipitation, warm anomalies above roughly 500 hPa, cold anomalies between roughly 500-700 hPa and cold anomalies near the surface were observed at most precipitating groups (PRG1-PRG5) at every station (not shown). These anomalies were most likely the result of diabatic heating in the anvils of mesoscale convective systems (MCSs) above roughly 500 hPa, cooling due to evaporation of precipitation falling from the anvils of MCSs between roughly 500-700 hPa and cold pools due to convective-scale downdrafts near the surface, respectively.

The results also revealed that robust lower tropospheric warm anomalies between roughly 800-950 hPa, to which the rest of this text mainly focuses on, occurred over some stations while being absent over others. Figure 1 shows that over stations with smaller climatological mean relative humidity at 500-700 hPa, lower tropospheric warm anomalies at 850 hPa were observed and that the magnitude of the warm anomaly was larger with larger amount of previous precipitation. Over stations with larger 500-700 hPa climatological mean relative humidity, the warm anomalies were absent even after large amounts of previous precipitation (Figure 1). Figure 1 also shows that over all stations, a cold anomaly at 600 hPa, above the 850 hPa warm anomaly, was observed after precipitation.

![Figure 1](image-url)

Figure 1. Temperature difference between each precipitation group and the piecewise mean at 850 hPa (left figure) and at 600 hPa (right figure) as function of the 500-700 hPa climatological mean relative humidity at each station. Colours represent the precipitation group (PRG0 ‘black’, PRG1 ‘blue’, PRG2 ‘purple’, PRG3 ‘dark red’, PRG4 ‘red’, PRG5 ‘yellow’). The markers corresponding to each station is shown in the right hand side legend. The lines are the least-squares fits.

Wei et al. (1998) observed that over the West Pacific the virtual temperature differences between cloud updrafts and the environment were roughly 0.5 K at 850 hPa. The 850 hPa temperature anomaly in the precipitating group with the largest amount of previous precipitation (PRG5) exceeds that of the non-precipitating group (PRG0) by roughly 0.5-1.3 K depending on the station (virtual temperature anomalies are of similar magnitude). Therefore, the warm anomalies we observed over the dry stations are large enough to significantly reduce the buoyancy of rising air parcels, and hence they may be detrimental for the formation of future deep convection.

That the lower tropospheric 800-950 hPa warm anomalies 1) occurred only over the driest stations, 2) were larger with larger amounts of previous precipitation and 3) were below a low-to-midtropospheric cold anomaly between 500-700 hPa, suggests that the warm anomalies were the result of subsidence below a layer of strong evaporation of stratiform precipitation falling from the anvils of MCSs. Hence, the
warm anomalies may provide a new mechanism, in addition to entrainment, to explain the relationship between deep convection and lower tropospheric moisture. Our results highlight the importance of accurately representing evaporation in numerical weather prediction and climate models in order to produce better weather and climate predictions.

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MEASUREMENTS OF THE EFFECT OF CLOUD PROCESSING ON AEROSOL CHEMICAL COMPOSITION

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Keywords: CLOUD PROCESSING, AEROSOL CHEMICAL COMPOSITION, MASS SPECTROMETRY

INTRODUCTION

Aerosol-cloud interactions remain as one of the most important sources of uncertainty in the current knowledge of aerosol radiative forcing. One of the aspects of aerosol-cloud interactions is cloud processing, i.e., how the formation of cloud droplets alters the chemical composition of ambient aerosol particle population. Furthermore, changes in aerosol chemical composition may result in significant changes in aerosol hygroscopicity, a property that is essentially linked to particles ability to act as cloud condensation nuclei as well as their optical properties (Väisänen et al., 2016; Zieger et al., 2015).

The mechanisms and different pathways of cloud processing are numerous. For example, a large fraction of the oxidation products of atmospheric volatile organic compounds is water-soluble allowing the partitioning into liquid cloud droplets. These compounds may further react in cloud water to form low-volatility organic compounds that remain in the particle phase after the cloud droplets evaporate (e.g., McNeill, 2015). On the other hand, the liquid interface may also initiate the uptake of inorganic species, such as $\text{SO}_2$ or $\text{HNO}_3$, that can further oxidize into less volatile aerosol phase compounds (e.g., $\text{H}_2\text{SO}_4$ and $\text{NH}_4\text{NO}_3$; Hayden et al., 2008; Harris et al., 2014).

METHODS

To study the effect of cloud processing on aerosol chemical composition, we organized an intensive measurement campaign at the Puijo measurement station in Kuopio, Finland, during the autumn 2016. The measurement station is located on the top floor of the 70-m tall tower reaching its top up to 240 m above the surrounding lake level. Therefore, it provides a unique opportunity to investigate the evolution of aerosol chemical composition in real atmospheric low-level clouds.

In addition to stationary aerosol instrumentation, the measurement station was equipped with three mass spectrometers. The bulk chemical composition of aerosol particles and cloud droplet nuclei was measured in real-time with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Additionally, the particle composition was measured with an iodide adduct chemical ionization mass spectrometer (iodide-CIMS) equipped with a FIGAERO inlet for particle phase measurements. Meanwhile, the gas phase composition was monitored with an additional iodide-CIMS operated without FIGAERO inlet.

By using the visibility and Ceilometer data, the measurement period was divided into cloudy and cloud-free sub-periods. A cloud event was considered to take place at Puijo when both the altitude of the lowest cloud layer and the visibility at the top of the tower dropped below 200 m. During cloud-free conditions, the altitude of the lowest cloud layer was more than 500 m. In addition, we estimated the origin of the air
masses by calculating 72-h back trajectories for each measurement hour with a HYSPLIT4 trajectory model.

PRELIMINARY RESULTS

According to an air mass trajectory analysis, majority of the observed cloud events were characterized by continental air masses arriving predominantly from southern and eastern directions. By contrast, cloud events occurred extremely rarely when the air masses arrived from either the North or West. Therefore, in this abstract, we concentrate only on continental cases in order to guarantee a representative set of observations for both cloud-free and cloudy conditions.

Figure 1 shows the results from positive matrix factorization (PMF) analysis applied to the AMS data. Shown are the organic mass fractions of hydrocarbon-like (HOM), semi-volatile (SVOOA) and low-volatile organic compounds (LVOOA) during cloud-free and cloudy measurement periods. Apparently, we observe slightly increased fractions of HOM and LVOOA during cloudy conditions, whereas SVOOA species have relatively stronger contribution during cloud-free conditions. This could indicate that cloud-processing favours the conversion of semi-volatile compounds to less-volatile species through aqueous phase oxidation.

The molar nitrate-to-sulphate ([NO$_3$]/[SO$_4$]) and ammonium-to-sulphate ([NH$_4$]/[SO$_4$]) ratios during cloudy and cloud-free periods are plotted as probability density distributions in Figure 2. The results indicate that both [NO$_3$]/[SO$_4$] and [NH$_4$]/[SO$_4$] are higher during in-cloud measurements compared to cloud-free periods. This could be explained by in-cloud neutralization of sulphate-containing particles together with enhanced uptake of HNO$_3$ that can lead to formation of NH$_4$NO$_3$ in cloud water.
CONCLUSIONS

We organized an intensive measurement campaign to investigate the effect of cloud processing on aerosol chemical composition. According to preliminary observations, we see differences in organic constituents with slightly increased contribution of low-volatile compounds during in-cloud conditions. In addition, we see cloud-condition dependent changes in nitrate-to-sulphate and ammonium-to-sulphate ratios. In future work we aim to combine the iodide-CIMS datasets (both particle and gas phase) with AMS observations and assess at the possible changes in organic and inorganic composition more detailed.

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FORMATION OF HIGHLY OXIDIZED MULTIFUNCTIONAL ORGANIC COMPOUNDS FROM CHLORINE RADICAL INITIATED OXIDATION OF A-PINENE

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ABSTRACT

Highly oxidized multifunctional organic compounds (HOMs) from oxidation of a-pinene in the atmosphere can irreversible condense to particles and contribute to secondary organic aerosol formation (Ehn et al., 2014). Recently, the formation of nitryl chloride (ClNO2) from heterogeneous reactions, and subsequent photolysis of nitryl chloride to produce chlorine atom is suggested to be extensive in the atmosphere (Thornton et al., 2010). However, the oxidation of monoterpenes such as a-pinene by chlorine radicals has received very little attention, and the ability of this reaction to form HOM is completely unstudied. Here, chamber experiments were conducted with a-pinene and chlorine gas under low NO and high NO conditions, respectively. A NO3-based CI-API-L-TOF was used to measure highly oxidized products. Simultaneously, other state-of-the-art instruments were used to measure other parameters in the chamber. Clear distributions of monomers with 9-10 carbon atoms and dimers with 18-20 carbon atoms were observed under low NO conditions. With increased concentration of NO in the chamber, the formation of dimers was suppressed due to the competition reactions of peroxy radicals with NO. We calculated the HOMs yields from chlorine-initiated oxidation of a-pinene under low NO conditions, while the yield at high NO could not be determined because of interference from ozone produced from the NOx, which subsequently reacted with a-pinene. Our study demonstrates that chlorine radical initiated oxidation of a-pinene will produce low volatility organic compounds, especially these HOMs, which indicates that autoxidation processes in chlorine radical oxidation of a-pinene will be important (Crounse et al., 2013). Further analysis will provide insights on the expected importance of the studied reactions in the atmosphere.

REFERENCES


2014.
EXPERIMENTAL INVESTIGATION OF AEROSOL PARTICLE COMPOSITION AND GROWTH RATES

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Keywords: nanoparticles, CPC battery, new particle formation.

INTRODUCTION

The chemical composition of naturally charged and neutral clusters can be determined using high resolution mass spectrometry. Clusters with masses up to roughly 1000 amu (=2 nm in mobility) can be chemically analysed with high resolution. The limitations of the high-resolution mass spectrometry comprise the selective charging (mostly nitrate ions are used as reagent, Jokinen et al., 2012), the limited upper size range and the quantification of the measurements. When studying new particle formation phenomena, the chemical composition and the formation rates of aerosol particles between 1.5 and 3 nm are crucial (Kulmala et al., 2014). Even though smaller clusters can exist, their relevance is determined by whether those clusters grow to larger sizes or not. Here we present a simple method to determine aerosol particle chemical composition and their growth rates. The instrument design is aimed at bridging the size gap between high resolution mass spectrometry and other mass spectrometers which are used for quantifying the chemical composition of aerosol particles starting from around 5 nm in mobility diameter.

METHODS

In this work, we present a measurement technique to indirectly determine the particle composition for the size range between 2 to 10 nm. The particle growth rates can also be measured directly. The instrument consists of at least three different ultrafine CPCs, each using a different working fluid. The liquids used are water, butanol and DEG. The CPCs used in the CPC battery are tuned to the smallest sizes possible without generating homogeneous nucleation background in the instrument itself following a similar procedure as in Kuang et al., 2012. A similar device has been used already previously, showing that the hygroscopicity of the aerosol particles can be resolved (Kulmala et al., 2007). Upstream of the CPC battery, a Differential Mobility Analyser (DMA) is used. Using a DMA has two advantages. First, the particle growth rates can be determined. Second, as the diameters are fixed at any given time during the measurement cycle, the detected signal in each CPC can be attributed to the interaction between the aerosol particle and the condensing liquid. This together with the results from the characterization in the laboratory allows for indirect determination of the chemical composition of the aerosol particles.

Various studies have shown that the activation efficiency of an ultrafine CPC strongly depends on the interaction between the condensing liquid and the chemistry of the aerosol particles that are measured (Iida et al., 2009). The results in Kangasluoma et al., 2014, showed that salt like aerosol particles are activated easier with the water based CPC compared to the butanol based CPC. The opposite was true for the other aerosol particle types (e.g. limonene ozonolysis products). By carefully characterizing the CPCs in the laboratory using different aerosol particle types, their response with respect to aerosol particle
composition is explored. This data will be used for inferring the chemical composition of the aerosol particles when the instrument is deployed for field measurements.

FIELD MEASUREMENTS

We will present preliminary field results. The instrument was deployed at the Hyytiälä field station during spring 2013. In addition to the data retrieved from the nano-CPC battery, the Hyytiälä station also provides other sub-3 nm aerosol particle size distribution and total concentration data. Mass spectrometer data for the smallest clusters is also available there, which allows to follow the nucleation and growth of the aerosol particles starting from the smallest clusters to larger (>10nm) sizes. In addition to that, comprehensive measurements of various trace gases, such as SO$_2$, O$_3$ and NO$_x$ are available which support the data that we will gather and help to understand better the processes attributed to the new particle formation.

ACKNOWLEDGEMENTS

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REFERENCES


THE ATMOSPHERIC FATE OF MONOETHANOLAMINE: ENHANCING NEW-PARTICLE FORMATION OF SULFURIC ACID AS AN IMPORTANT REMOVAL PROCESS

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INTRODUCTION

Monoethanolamine (MEA, NH2CH2CH2OH) is a benchmark and widely utilized solvent in amine-based postcombustion CO2 capture (PCC) technology. Given the possible large-scale implementation of amine-based PCC, it is likely that there will be relatively significant emissions of MEA or other alkanolamines to the atmosphere from PCC units due to their relatively high vapor pressure.1 It has been estimated that a CO2 capture plant which removes 1 million tons CO2 per year from flue gas using MEA as solvent could potentially emit 80 tons MEA into the atmosphere.2 Therefore, in recent years concern about the atmospheric fate of the representative amine MEA has been increasing,3 as MEA could potentially form an environmental risk.2 Several studies have addressed the removal of MEA by atmospheric oxidation.3

Besides oxidation, acid-base reaction could be another important sink for MEA. However, the atmospheric fate related to the basicity of MEA has received little attention until now.

Atmospheric aerosol particles, at least 50% of which originates from new-particle formation (NPF), are known to affect human health and remain one of the leading uncertainties in global climate modeling and prediction.4,5 Many studies have shown that atmospheric bases such as ammonia and amines stabilize sulfuric acid clusters in the lower troposphere via acid-base reactions, and therefore enhance H2SO4-based NPF rates.6 Compared to ammonia, amines, including monomethylamine (MA), dimethylamine (DMA) and trimethylamine (TMA), can bind much more strongly to sulfuric acid molecules and thus can efficiently enhance clustering sulfuric acid.4

In a similar fashion to simple alkylamines, MEA can potentially influence NPF via acid-base reactions and therefore participating in NPF could be another atmospheric sink of MEA. A recent study highlighted the possible role of emitted amines from CO2 capture unit of PCC in enhancing NPF.4 The basicity of MEA is higher than that of ammonia and lower than that of methylamine and dimethylamine (pKb values of MEA 4.50, MA 3.36, DMA 3.29, ammonia 5.7).6 If judged solely by the basicity, MEA should have a higher enhancing effect on H2SO4-based NPF than NH3, and lower effect than MA and DMA when atmospheric concentration of MEA is assumed to be similar to that of NH3, MA and DMA. From the point of molecular structure, MEA has additional -OH compared to ammonia, MA and DMA. When forming clusters between MEA and H2SO4, the -OH group in MEA can form additional hydrogen bonds (H-bonds), which increase the binding energy of MEA with H2SO4. The conflicting effects of one favorable (more H-bonds) and one unfavorable factor (decreased basicity compared with methylamine and dimethylamine) could make it difficult to estimate how strong the enhancing effect of MEA will be. No previous studies have considered the potential role of alkanolamines in NPF involving H2SO4. An additional -OH in the amine may lead to a different NPF pathway and rate compared to the ammonia/MA/DMA-H2SO4 systems. Therefore, to obtain a complete view of the atmospheric fate of MEA and extend the current knowledge of NPF involving amines and H2SO4, information about the
potential of MEA to participate in atmospheric NPF is crucial.

In this study, we investigate the initial step of atmospheric H$_2$SO$_4$-based NPF by examining the formation of molecular clusters of MEA and sulfuric acid using a combination of quantum chemistry calculations and kinetics modeling employing the Atmospheric Cluster Dynamics Code$^2$ (ACDC). Via systematic conformational searches, we have obtained minimum free energy structures of clusters of composition (MEA)$_m$(SA)$_n$ ($m=0$-$4$ and $n=0$-$4$, “SA” represents H$_2$SO$_4$). The corresponding thermodynamic data and previously reported results for pure sulfuric acid (SA)$_4$ clusters$^8$ are used in ACDC to obtain cluster formation pathways and kinetics in the MEA-H$_2$SO$_4$ system. In addition, the effect of hydration on the cluster formation kinetics of MEA and H$_2$SO$_4$ is considered.

METHODS

Here, a global minimum sampling technique (Figure 1), which has previously been applied to study atmospheric cluster formation,$^6$ was used to search for the global minima of clusters (MEA)$_m$(SA)$_n$($m=1$-$4$ and $n=0$-$4$) and hydrated clusters (MEA)$_m$(SA)$_n$W$_x$ ($m=0$-$2$, $n=0$-$2$, $x=1$-$3$, “W” represents H$_2$O). The pure (SA)$_4$ clusters were taken from the work of Ortega et al.$^8$ In addition, to directly compare the enhancing effect of MEA to ammonia, MA and DMA, we re-evaluated their formation free energies at the same theoretical level, based on reported cluster structures, or new lower energy structures.$^8,11$ We used ACDC to study the formation pathways, steady-state concentrations and formation rates of clusters.

![Flowchart](image)

**Figure 1.** Flowchart for the multistep global minimum sampling method. “SP” represents a single point energy calculation.

CONCLUSIONS

We found that MEA at ppt-level can enhance H$_2$SO$_4$-based NPF. The enhancing potential of MEA is < dimethyamine (DMA), one of the strongest enhancing agents, and $\gg$ methyamine (MA), in contrast to the order suggested solely by their basicity (MEA < MA < DMA). The unexpectedly high enhancing potential is attributed to the role of -OH of MEA in increasing cluster binding free energies by acting as both hydrogen bond donor and acceptor. After the initial formation of one H$_2$SO$_4$ and one MEA cluster, the cluster growth mainly proceeds by first adding one H$_2$SO$_4$, and then one MEA, which differs from growth pathways in H$_2$SO$_4$-DMA and H$_2$SO$_4$-MA systems. Importantly, the effective removal rate of MEA due to participation in NPF is comparable to that of oxidation by hydroxyl radicals at 278.15 K, indicating NPF as an important sink for MEA.
ACKNOWLEDGEMENTS

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REFERENCES

GROWTH AND VOLATILITY OF NANOPARTICLES AT HYYTIÄLÄ IN SPRING 2014

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Keywords: ORGANICS, SOA, GROWTH, ATMOSPHERE.

INTRODUCTION

Freshly formed atmospheric secondary aerosol particles have diameters of the order of nanometers. Growth of these nanoparticles has potential to produce large numbers of climatically relevant aerosol particles (Merikanto et al., 2009). While the growth of nanoparticles is observed frequently in various atmospheric environments (Kulmala et al., 2004), the mechanisms related to the growth and the identity of the participating species are not known yet in detail. This produces uncertainty in estimates of aerosol-cloud interaction and, consequently, in climate predictions.

Oxidation of various atmospheric organic trace gases produces a multitude of species, some of which are low enough volatile to condense on nanoparticles and thereby grow them in size (Hallquist et al., 2009). The variety of the relevant species and their low concentrations in ambient air casts challenges in detecting them, which complicates the investigations of nanoparticle growth processes. Addition to the organics, inorganic compounds, especially sulphuric acid and ammonia, are likely contributors to nanoparticle growth. Therefore, atmospheric nanoparticle may be complex mixtures with various potential factors that limit their growth (Riipinen et al., 2012).

Mohr et al. (2017) investigated dimeric monoterpen oxidation products based on measurements of organic species in Hyytiälä, Finland. In this study, we utilize partly the same data set and take a detailed look at the nanoparticle growth process. We investigate the growth of atmospheric nanoparticles by simulating the condensation of detected gas phase compounds on a freshly formed aerosol particle. We compare the simulated particle growth rate and composition to the measured time evolution of particle size distribution and to the measured nanoparticle volatility.
METHODS

We investigated nanoparticle growth events detected in the boreal forest at SMEAR II station, Hyytiälä, Finland, during April-May 2014. Gas phase concentrations of organic species were measured with a chemical ionization high-resolution time-of-flight mass spectrometer with a filter inlet for gases and aerosols (FIGAERO-CIMS), using iodide as the reagent ion. These measurements gave the time series of the gas phase concentration of each detected organic species and the corresponding molecular formula. Saturation concentration ($C_{sat}$) of each species was calculated according to Donahue et al. (2011), a parametrization based on the number of carbon, oxygen and nitrogen atoms in the species. The organic compounds were then presented in terms of a 1-D volatility basis set (VBS) with factor of 10 difference in $C_{sat}$ between the bins (up to 17 bins). In addition to the organic compounds, measured gas phase concentrations of sulphuric acid and ammonia, and relative humidity and temperature were used as inputs for the model simulations (see Mohr et al., 2017 and references therein for details of the measurements).

Growth of a nanoparticle was simulated with the MABNAG model (Model for acid-base chemistry in nanoparticle growth; Yli-Juuti et al., 2013) assuming that the condensing species were the organics (presented with the VBS), sulphuric acid, ammonia and water. MABNAG simulates the changes in particle size and composition given the surrounding gas phase conditions and taking into account acid-base chemistry inside the particle. The model was initialized with a particle that consisted of 40 sulphuric acid molecules and an amount of ammonia and water that corresponds to gas-particle equilibrium.

The change in nanoparticle size predicted with the model was compared to the evolution of particle size distribution measured with a differential mobility particle sizer (DMPS). Predicted nanoparticle composition was compared to the observed volatility of 30 nm particles, which was measured with a volatility tandem differential mobility analyser (VTDMA; Hong et al., 2017). For this, the predicted particle composition at 30 nm was used as an input to simulations of particle evaporation in a VTDMA (Riipinen et al., 2010), and the resulting simulated changes in particle size at different temperatures were compared to the observations.

RESULTS AND CONCLUSIONS

The detected gas phase concentrations of condensable compounds were high enough to explain the observed nanoparticle growth, as the model somewhat overestimated particle growth rate. Majority of the simulated particle growth was due to condensation of low-volatile (LVOC) and extremely low-volatile organic compounds (ELVOC), and nitrate containing compounds contributed significantly. The simulated particle composition, in terms of the volatility distribution, agreed on average well with the VTDMA measurements suggesting that the nanoparticle composition was adequately captured in the model in spite of the overestimation of the growth rate. The comparison of the model simulations to both the observed particle growth and volatility allowed investigating the sensitivities to the uncertainties in measured gas concentrations, estimated $C_{sat}$ and other properties. We also investigated to possibility to simplify the presentation of the organics by including fewer VBS bins. While the simulated growth was not sensitive to separating the ELVOCs based on their $C_{sat}$, comparison to volatility measurements required detailed separation.

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REFERENCES


INTRODUCTION

Secondary Organic Aerosol (SOA) particles formed from volatile organic compounds (VOCs) are composed of a large number of different chemical compounds with different functional groups (Hallquist et al. 2009.). The chemical fingerprint of each particle and thus its physical properties are determined by the initial emissions of VOCs and the oxidative conditions they experience (Glasius and Goldstein 2016). One of the physical properties determining the fate of SOA particles in the atmosphere is the volatility of the organic compounds. Depending on the gas phase concentration, low volatile compounds can evaporate from the particle phase changing the composition and size of the particles. These changes can impact the cloud droplet formation ability of the SOA particles and thus have an impact on climate.

METHODS

In this study, we used the Filter Inlet for Gases and AEROsols – Time of Flight – Chemical Ionization Mass Spectrometer, (FIGAERO-ToF-CIMS, Lopez-Hilfiker et al., 2014) with iodide ionization to investigate the chemical differences of SOA generated from the oxidation of α-pinene or from real Scots pine emissions in a Potential Aerosol Mass reactor (Kang et al., 2007, Lambe et al., 2011) The emissions from a Scots Pines were monitored online with Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) and offline with Gas Chromatography – Mass Spectrometry (GC-MS). Particles formed inside PAM were monitored with Aerodyne Aerosol Mass Spectrometer (AMS) and the size distribution was measured with Scanning Mobility Particle Sizer (SMPS, TSI Inc.). The experimental setup can be seen in Figure 1. Mass spectrometry data from FIGAERO-ToF-CIMS was processed using program tofTools (Junninen et al. 2010). Data is then to be further analyzed with Positive Matrix Factorization-toolkit (Ulbrich et al., 2009) in the future.
For α-pinene emissions the PAM-reactor was used to produce three different oxidative conditions termed “low”, “medium” and “high exposure” which corresponded roughly 2, 5 and 19 days of oxidative age in the atmosphere. As Scots Pine emissions were varying with time, the PAM-reactor was used with fixed oxidative conditions for four different experiments, which corresponded to roughly 5 days of oxidative aging.

RESULTS AND CONCLUSIONS

In Figure 2, upper two panels shows integrated mass spectra from medium exposure α-pinene experiment and from one Scots Pine experiment, both having oxidative age of roughly 5 days. Lower panel shows normalized Total Ion Count (TIC) thermograms (total signal vs. evaporation temperature) from each α-pinene experiment and one Scots Pine experiment corresponding to mass spectra shown in the upper right panel.

The results show clearly how peak value of the TIC changes to higher temperatures as the oxidative age of the SOA particles increase in the α-pinene experiments. It is also worth noting that even though the oxidative age of SOA formed from Scots Pine emissions is shorter relative to high exposure SOA from α-pinene emissions, it still has the highest peak evaporation temperature. This implies that SOA formed from Scots Pine emissions is less volatile than in any case of α-pinene experiments. The results also cast doubt to widely used assumption that α-pinene can be used as proxy for emissions from boreal forests, even though emission profiles from seedlings and grown up trees might differ.
Figure 2. Upper two panels show integrated mass spectra from medium exposure α-pinene experiment and from one Scots Pine experiment. Both experiments have similar oxidative age of roughly 5 days. Lower panel shows normalized Total Ion Count thermograms from each α-pinene experiment and from same Scots Pine experiment as shown in the upper right panel.

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REFERENCES


TESTING OF TRACE GASES AND AEROSOL MASS CONCENTRATION MEASURING ENVITEMS SENSORS AT SMEAR II STATION

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Keywords: AIR QUALITY MONITORING, INSTRUMENT COMPARISON, ENVITEMS, SMEAR II.

INTRODUCTION

The air quality monitoring is important because trace gases and aerosols lead to impaired living conditions causing health problems and deaths (Stocker et al., 2014). A Finnish company called Envitems has brought to market Envitems E4100 air quality monitor. It is designed to the areas where air quality is degraded and a versatile monitoring is needed. It measures atmospheric particulate matter (PM) mass concentration in two different size classes: PM$_{10}$ that is particles with diameter smaller than 10 µm and PM$_{2.5}$ that is particles with diameter smaller than 2.5 µm. It can measure simultaneously four of the following trace gases: nitrogen monoxide (NO), nitrogen dioxide (NO$_2$), ozone (O$_3$), carbon monoxide (CO), carbon dioxide (CO$_2$), sulphur dioxide (SO$_2$), hydrogen sulphide (H$_2$S) and volatile organic compounds (VOC). Sensor measures three meteorological variables: air temperature, ambient pressure and relative humidity (RH).

Two Envitems E4100 sensors were installed at SMEAR (Station for Measuring Ecosystem-Atmosphere Relations) II station in Hyytiälä in southern Finland. To test the functioning of the sensors, their results were compared with the research level instruments observing the atmosphere continuously. The data was collected between July 25th and September 21st in 2016. Envitems sensors are referred as 770 and 771 according to manufacturer’s serial numbers. The sensor 770 was installed about 6 m height to the roof of the so called Hitu cottage in which the main aerosol instrumentation is located. The sensor 771 was measuring at 33.6 m height at the measurement mast. Installed sensors monitored first four of the listed gases, that is NO, NO$_2$, O$_3$ and CO.

METHODS

Atmospheric PM$_{2.5}$ data was compared with mass concentration data derived from size distribution measurements. Combination of Differential Mobility Analyser System (DMPS) and Aerodynamic Particle Sizer (APS, TSI 3321) data was applied for covering the aerosol concentration in the size distribution scale required for calculating PM$_{2.5}$ (Aalto et al., 2001; Volkens and Peters, 2005). DMPS scans size distribution between 3 nm and 1 µm, and measurement range of APS is 0.5 - 20 µm on aerodynamic diameter. After converting aerodynamic diameter to Stoke’s diameter APS data can be used for extending the size distribution to 2.5 µm. Along with size distribution data, PM$_{10}$ data was also compared with online mass measurements from Synchronized Hybrid Ambient Real-time Monitor (SHARP, Thermo Fisher Scientific 5030).

The size distribution data was inverted to mass distribution by multiplying the volume of one particle with its density $\rho$

\[ m = \frac{4}{3} \pi \rho \left( \frac{d}{2} \right)^3. \]  

In the formula $d$ means the diameter of the particle. Particles were assumed to be spherical and that their density equal to 1.5 kg/m$^3$ (Kannosto et al., 2008).
At SMEAR II station gases are measured in the high (125 m) mast at many levels. The Envitems sensor 770 was compared with continuous measurements at altitudes 4.2 and 8.4 m and sensor 771 with the level of 33.6 m measurements as they are the corresponding altitudes. In the mast Thermo Electron Corporation 42i Trace Level analyser monitors nitrogen monoxide and NO\(_x\), ergo a combination of nitrogen monoxide and nitrogen dioxide. Nitrogen monoxide is measured also at 35 m high tower with Eco Physics CLD 780 TR analyser. Its results are compared to both Envitems sensors. Because it is more sensitive than the Thermo Electron Corporation’s analyser, its NO value was used when calculating NO\(_2\) from NO\(_x\) data. Ozone analyser at SMEAR II station is Thermo Electron Corporation 49C and Teledyne Advanced Pollution Instrumentation 300EU analyser is used for carbon monoxide measurements.

The ambient air pressure is measured with General Eastern Instruments DPI260 barometer. Temperature is measured in a ventilated and radiation-shielded casing with PT-100 sensors. Two different data sets are used as RH reference data: direct RH measurements with Rotronic MP102H analyser with Hygroclip HC2-53 sensor from a tower at 16 m altitude, and secondarily it can be derived from PT-100 sensor’s temperature and Li-Cor LI-840 sensor’s water concentration measurements. Temperature and the latter RH data are from the same levels as gas measurements.

Before starting the measurements Envitems sensors were stabilized for 24 hours along with the manufacturer’s instructions. Data from Envitems sensors was plotted against reference data from SMEAR instrumentation to analyse their correlation. Pearson’s correlation was applied for quantify the level of agreement with different instruments.

**CONCLUSIONS**

The calculated correlation coefficients from the aerosol mass concentration measurements are shown in Table 1. In PM\(_{10}\) size class the coefficients are larger than in PM\(_{2.5}\). Compared to SMEAR II stations measurements Envitems sensors underestimate the mass concentration by few to over ten micrograms in a cubic centimetre. Sample volume in the Envitems sensors is small, only 0.1 litres. It may cause difficulties with the algorithms because air around the station is relatively clean and the aerosol particle number concentration is low. Mass concentration in Hyytiälä is only a little larger than the detection limit of the sensor. Thus the sample air contained too few particles for reliable estimate of the concentration for the E4100 sensor. On the other hand the differences were larger when the mass concentration was larger in Hyytiälä, which disagrees with the assumption that the small sample volume was the cause for the differences. Figure 1 shows correlation plot for Envitems 770 and SHARP monitor. Green line is 1:1 line and purple is a line fitted to data points (linear least squares fitting). The slope of the fitted line is and slope is 0.105 with y-axis interception of 0.0896 \(\mu\)m/m\(^3\). In the figure the underestimation of the Envitems sensor is seen. Pearson’s correlation coefficient was 0.129.

<table>
<thead>
<tr>
<th>Envitems</th>
<th>SHARP</th>
<th>APS+DMPS (<em>{PM</em>{10}})</th>
<th>APS+DMPS (<em>{PM</em>{2.5}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>770/771</td>
<td>0.129</td>
<td>0.112</td>
<td>0.0482</td>
</tr>
<tr>
<td>771</td>
<td>0.149</td>
<td>0.119</td>
<td>0.0445</td>
</tr>
</tbody>
</table>

Table 1. Pearson’s correlation coefficients for aerosol measurements.
Correlation coefficients from gas measurements are listed in Table 2. Of gas measurements ozone correlates most with the reference data as the coefficients with both sensors are between 0.804 and 0.833. Anyhow, both of the Envitems sensors estimate concentration to be 10 – 20 ppb higher. For carbon monoxide the coefficients are between 0.0751 and 0.279. From the data it could be seen that the noise in the measurement signal impaired the correlation. Furthermore, instruments functioned differently. Sensor 770 overestimated the carbon monoxide concentration in Hyytiälä and sensor 771 underestimated it. Magnitude of the differences was tens of parts per billions. Signal of the sensor 771 was between 0 and 20 ppb even though the carbon monoxide concentration during in Hyytiälä was about 100 ppb. Detection limit of the Envitems E4100 sensor was 10 ppb therefore it seems that sensor 771 may have measured only noise around the limit. Concentration of nitrogen oxides was below the 5 ppb detection limit of the Envitems sensor, and hence the quality of the measurement data cannot be estimated.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Envitems 770/771</th>
<th>Mast 33.6 m</th>
<th>Mast 8.4 m</th>
<th>Mast 4.2 m</th>
<th>Tower 35 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>770</td>
<td>-0.0003</td>
<td>0.0358</td>
<td>-0.0297</td>
<td></td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>-0.0363</td>
<td>-</td>
<td>-</td>
<td>0.0892</td>
</tr>
<tr>
<td>NO2</td>
<td>770</td>
<td>-0.0352</td>
<td>-0.0128</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>-0.206</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O3</td>
<td>770</td>
<td>0.807</td>
<td>0.833</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>0.804</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>770</td>
<td>0.0751</td>
<td>0.0933</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>0.279</td>
<td>-</td>
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<td>-</td>
</tr>
</tbody>
</table>

Table 2. Pearson’s correlation coefficients for gas measurements.

According to this study, for meteorological variables Envitems sensors correlated well with reference instruments. Correlation coefficient on ambient pressure measurements were 0.999. Even so, both of the sensors had a shift in correction factor compared to SMEAR II barometer due to which they overestimated the reading by about 7 mbar. Yet, sensors seem to function correctly as sensor 771 that is installed at
higher altitude than sensor 770 measures lower readings. Correlation coefficients in temperature were between 0.990 and 0.992 and in RH between 0.965 and 0.981. All the coefficients are listed in the Table 3.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Envitems 770/771</th>
<th>Mast 33.6 m</th>
<th>Mast 8.4 m</th>
<th>Mast 4.2</th>
<th>Tower 16 m</th>
<th>Ambient Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>770</td>
<td>-</td>
<td>0.991</td>
<td>0.992</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>0.990</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pressure</td>
<td>770</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.999</td>
</tr>
<tr>
<td>RH</td>
<td>770</td>
<td>-</td>
<td>0.981</td>
<td>0.981</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>771</td>
<td>0.979</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3. Pearson’s correlation coefficients of meteorological variables.

Test measurements were conducted at SMEAR II station in Hyytiälä as there is versatile long-term measurements of variables of interest, and measurement data is monitored on a daily basis. The relatively clean air around the station was challenging as the Envitems sensors has been designed for more polluted regions. Aerosol mass concentration and nitrogen oxide test measurements should be conducted in a urban area. On the other hand better aerosol mass concentration results may be attained by changing the inversion algorithm, but sensors should also be more sensitive. From the data it was seen that ozone measurements would need a longer time to stabilize due to slow adaptation of the algorithm. Also further investigation is needed to understand why Envitems sensors’ results in carbon monoxide concentration differ widely from another. A lower detection limit of nitrogen oxides is needed to enable concentration measurements in many more cities.

ACKNOWLEDGEMENTS

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BAYESIAN CLASSIFICATION OF TIME SERIES FEATURES FOR PREDICTING ATMOSPHERIC PARTICLE FORMATION DAYS

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Keywords: ATMOSPHERIC AEROSOL PARTICLES, NEW-PARTICLE FORMATION, MACHINE LEARNING, BAYESIAN NEURAL NETWORKS

INTRODUCTION

Atmospheric aerosol particles are minute molecular agglomerations suspended in the air. These small particles take part in a multitude of physical processes, some of which have very heavy societal impact: among these are the loss of visibility and harmful health effects — and even climatic consequences via aerosol-cloud interactions (Langridge et al., 2012). Atmospheric scientists are thus interested in understanding how various processes modify the properties of aerosol particles and especially how, why and when these particles form. However, the paths leading to atmospheric aerosol particle formation are not yet completely understood due to the vast physical and chemical complexity of the atmosphere. One straightforward approach to overcome this issue is to gather more data from the atmosphere.

Towards this end, several Stations for Measuring the forest Ecosystem-Atmosphere Relationships (SMEAR) have been established in Finland. These stations measure a large number of atmospheric variables, such as gases, meteorology, radiation, aerosol particles and soil fluxes at different altitudes. At SMEAR II station in Hytyiä forest alone (Hari and Kulmala, 2005), there are hundreds of observables in total since 1996 (i.e. millions in sample size), producing big data. The measurement of ambient aerosol size distributions is typically used to identify periods of new particle formation (NPF) growth (event days) and days when no particle formation is observed (non-event days). The NPF event days can be further divided into class I and class II based on their confidence level. Class I is assumed when the growth and formation rate can be determined with a good confidence level, whilst class II occurs when the derivation of these parameters is not possible or there is a doubt in the accuracy of the results. Class I can be still further divided into sub-classes Ia and Ib. Class Ia is assumed when the day shows a very clear and strong particle formation event, with very little or no pre-existing particles obscuring the newly-formed mode, whereas class Ib contains the remaining class I events. An example of four different types of NPF days is shown in Figure 1. Manual labor with such multi-years data for determination of event/non-event days is a challenging task and thus robust automated procedures for data analysis are called for (Kulmala et al., 2012).
In this study, we present a Machine Learning (ML) based Bayesian neural network (BNN) to automatically classify the days only into event and non-event days. The sub-classification of NPF days provides useful information while analysing the result of the classification performance.

**METHODOLOGY**

Aerosol particle concentration data from Differential Mobility Particle Sizer (DMPS) instrument is pre-processed first before it is fed into the ML model. From this data, the features can be calculated and extracted before it is fed to an ML model. The ML output is a list of event and non-event days based on expert visualization (Dal Maso *et al.*, 2005). Figure 2 illustrates the block diagram of the proposed classification strategy. In the first step, the particle concentrations (at the range of 3 nm-1000 nm) are pre-processed to extract only useful data. In this step, we remove outlier data, which may contain suspicious data due to sensor fault or extreme conditions. Evening time periods for each day are also excluded because typically new-particle formation occurs during the day time (Hyvönen *et al.*, 2005).

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**Figure 1:** Four different types of NPF days, classified based on the method proposed by Dal Maso *et al.* (2005). The x-axis shows the 24-hours time period whereas y-axis represents the range of particle diameters (from 3 nm to 1000 nm). The color indicates the particle concentration (cm$^{-3}$).

**Figure 2:** Machine Learning classifier methodology used in this work.
In the next step, we calculate two types of necessary features used in the analysis. Aerosol particle size distributions are fitted with a multi-modal Log-Gaussian distribution function using automatic algorithm developed by Hussein et al. (2005). The properties of the multi-modal Log-Gaussian distributions are taken as the first type of features. The second type of features are the time domain properties of particle concentrations, such as mean, standard deviation, kurtosis and skewness. The features representation are illustrated in Figure 3. These features are computed from two different directions of “banana plot” and this strategy should provide the richness in the feature information for ML model to distinguish between event and non-event days.

Figure 3: Two types of features are calculated. First feature is the properties of multi-modal Log normal distribution whereas the second features are computed from the time-domain representation.

The combination of these features results in a large number of feature dimension which may lead to the *curse of dimensionality*: ML algorithms perform poorly with high-dimensional data (Bishop, 2006). This motivates the use of dimensionality reduction techniques, such as Principal Component Analysis (PCA). Thus, we project all of the obtained features using PCA onto Principal Components (PCs) space. We then extract only some of the highest variance PCs to be used as the inputs of BNN classifier in the last step. As shown in Figure 4, after several validation procedures, we use BNN with one hidden layer containing 25 neurons to perform classification (Hagan et al., 2014).

Figure 4: The structure of Bayesian neural network classifier used in this work.
We divide the data into two different parts: training and testing data. We use the data from 1996-2010 as training data whereas the period of 2011-2014 is used as testing data. The training data is fed into BNN classifier for optimizing its weights. The use of Bayesian inference for neural network is to avoid over-fitting during the training phase due to the presence of regularization. The result of the training process is presented as a confusion matrix in Table 1. This metric presents the BNN accuracy over the manual visualization method (i.e. the target data set). It can be seen that the network training has a classification accuracy of 97.9%, indicating that the training process was very successful.

<table>
<thead>
<tr>
<th>BNN</th>
<th>Visualization Method</th>
<th>Event-Days</th>
<th>Non-Event Days</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Event-Days</td>
<td>1223 (42.0%)</td>
<td>29 (1.0%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-Event Days</td>
<td>32 (1.1%)</td>
<td>1630 (55.9%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>97.5%</strong></td>
<td><strong>98.3%</strong></td>
<td><strong>97.9%</strong></td>
</tr>
</tbody>
</table>

Table 1: Training performance (1996-2010)

Once the training process is completed, the trained BNN classifier is then fed with testing data. The classification outcome is then compared with the target data set to evaluate the performance. The result is shown in Table 2. The method has a classification accuracy of 84.2% for determining event/non-event days using only aerosol particle concentration data from DMPS instrument. In other words, the BNN classifies automatically event/non-event days from 2011-2014 with the accuracy of 84.2%. In this case, the accuracy performance reduces from the training phase because the trained model may still experience over-fitting or the selected features might not represent well the particle concentrations needed for analysis.

<table>
<thead>
<tr>
<th>BNN</th>
<th>Visualization Method</th>
<th>Event-Days</th>
<th>Non-Event Days</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Event-Days</td>
<td>245 (30.3%)</td>
<td>63 (7.8%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-Event Days</td>
<td>65 (8.0%)</td>
<td>435 (53.8%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>79.0%</strong></td>
<td><strong>87.3%</strong></td>
<td><strong>84.2%</strong></td>
</tr>
</tbody>
</table>

Table 2: Validation performance (2011-2014)

![Figure 5: The bar chart of the successful and unsuccessful number of predicted days.](image)
Figure 5 presents the details of validation result. The bar charts display the number of days that are predicted successfully and unsuccessfully. It can be seen that BNN predicts all of classes Ia days successfully (100% accuracy). Class Ia is the group with clear NPF days and BNN success predicts all of them. In addition, BNN is still able to predict reasonably well for class Ib, that is about 85% (92 days) of successful rate. However, the method predicts correctly only 75% (146 days) of class II. The misclassified event day takes place mostly on the group of class II. This situation may occur because when the aerosol formation days database was generated (based on Dal Maso et al. (2005)), the accuracy of class II data was questionable. Like visualization method, BNN model may not be able to distinguish well between the class II and non-event group. Similarly, the failed prediction of non-event days, that is 13% (63 days), occurs due to the BNN confusion in differentiate between class II and non-event days. Nevertheless, we would say that BNN estimates non-event days (87%) reasonably well.

In conclusion, from the result analysis, it gives an indication that the ML method is promising for classifying automatically aerosol formation days. The developed ML model is adequate to provide rapid estimation for event/non-event days. This may speed up analysis, especially in research stations where there has been no database of aerosol formation days.

REFERENCES


VERTICAL CHARACTERIZATION OF HOMS ABOVE AND BELOW BOREAL FOREST CANOPY

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Keywords: HOM chemistry, Micro-meteorology, Planetary boundary layer

INTRODUCTION

Highly oxygenated molecules (HOMs) have been suggested to play a critical role in new particle formation (NPF) and secondary organic aerosol (SOA) formation [Bianchi et al., 2016; Ehn et al., 2014; Kulmala et al., 2013; Riipinen et al., 2011], which have strong influence on global climate change and radiation budget [Hallquist et al., 2009; Merikanto et al., 2009]. It is recognized that HOMs are formed via the oxidation of volatile organic compounds (VOCs) but the exact HOM chemistry in the real atmosphere still remains poorly understood. On one hand, the roles of different groups of HOMs (e.g. HOMs with/without nitrogen) in NPF and SOA formation are complicated and may vary significantly. On the other hand, their formation pathways and fate remain need investigation and may be altered with the changing environment conditions. HOMs measurements have been done in a few locations, however, due to the absence of vertical measurement, the influence from micro-meteorology and planetary boundary layer (PBL) dynamics to HOM chemistry are less understood.

During the Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen budget (IBAIRN) campaign in Hyytiälä, Finland, HOMs were for the first time measured and compared at different heights with two nitrate ion based Chemical Ionization Atmospheric Pressure-interface Time-of-flight mass spectrometers (CI-API-TOF) [Jokinen et al., 2012], which offered us a good opportunity to investigate the micro-meteorology and PBL influence on HOM chemistry.

INSTRUMENTATION

The University of Helsinki deployed three nitrate ion based chemical ionization atmospheric-pressure-interface time-of-flight mass spectrometers (CI-API-TOF) [Jokinen et al., 2012]in the IBAIRN campaign. Two of them are installed in different heights (ground level and 35m height tower) to measure the concentrations and vertical profile of HOMs and sulfuric acid. VOCs are measured with a proton transfer reaction mass spectrometer(PTR-MS) mass spectrometer [Graus et al., 2010]. Trace gases including CO₂, NOₓ, and O₃ are measured at different heights (4.2 m, 8.4 m, 16.8 m, 33.6 m, 50.4 m, 67.2 m, 125 m) on a 126 m mast ~100 m away from the tower
CONCLUSIONS

The HOMs concentrations were found similar above and below canopy during daytime. However, ground HOMs concentrations were much lower at ground level during nighttime (shown in Figure 1). Further analysis suggested that micro meteorology and PBL dynamics might play key roles in HOM chemistry at ground-level. Both HOM formation (lower concentrations of oxidants) and sink (higher probability of uptake on ground surface) were strongly influenced. A manuscript is under preparation based on the results.

Figure 1. Mean mass spectra of CI-API-TOF during selected daytime (09:00-15:00 local time) and nighttime (21:00-03:00 LT) periods. Bars in green stand for the measurements at ground level, bars in brown are the measurements on tower top (HOMs, 35m).

ACKNOWLEDGEMENTS

The authors would like to thank all staff at Hytyiälä forestry field station for the technical support. This work was partially funded by the European Research Council (Grant 638703-COALA), Academy of Finland (1251427, 1139656, Finnish center of excellence 1141135), European commission actris2 and actris PPP, transnational access from ENVRIplus. We also thank the tofTools team for providing tools for mass spectrometry analysis.

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Keywords: BVOC, dry deposition model, boreal canopy, emissions.

INTRODUCTION

A multi-layer BVOCs (Biogenic Volatile Organic Compounds) dry deposition model was implemented into a chemical transport column model SOSAA (Boy et al., 2011) to investigate the in-canopy exchanges of BVOCs between air and vegetation. Several deposition models for BVOCs were proposed two decades ago (e.g. Wesely, 1989). However, only until recently the detailed single-layer BVOC deposition models have been applied to investigate the BVOCs fluxes (Nguyen et al., 2015) and the loss of secondary organic aerosol (SOA) (Hodzic et al., 2014). The newly implemented multi-layer BVOCs deposition model in this study has provided a new insight on the BVOCs exchange of boreal forest. The new parametrization method can also be applied in large-scale models.

METHODS

The gas dry deposition model was based on the ozone dry deposition model described in Zhou et al. (2017). For BVOCs, the parametrization method for mesophyll resistance, cuticular resistance, soil resistance and wet skin resistance were extended from Wesely (1989) and Nguyen et al. (2015). The Henry’s law constants of all species included in current chemistry scheme were obtained from the measurement data if available (Sander, 2015), otherwise they were computed by the software EPI Suite v4.11 (https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface) with group method or bond method. The reactivity factors were taken from three values 0 (non-reactive), 0.1 (semi-reactive) and 1 (reactive), which were proposed according to the functional groups of organic compounds (Wesely, 1989; Karl et al., 2010). BVOC emissions were calculated by MEGAN (Guenther et al., 2006) with the standard emission potentials (SEPs) derived from measurement data in previous studies. The SEPs of separate monoterpenes were obtained from their average emission spectra (Bäck et al., 2012).

Twelve representative compounds were selected to analyse their sources and sinks within the canopy. Monoterpenes, isoprene+MBO, methanol, acetaldehyde, acetone and formaldehyde were chosen to verify the model by comparing their modelled and measured fluxes above the canopy. These seven compounds along with the sesquiterpenes constituted the majority of the emitted gases from the ecosystem at SMEAR II. Acetol was selected as a typical carbonyl compound, together with acetaldehyde, acetone and formaldehyde. Four highly oxidised organic compounds, including pinic acid oxidized from alpha-pinene, BCSOZOH oxidized from beta-caryophyllene, ISOP34NO3 and ISOP34OOH oxidized from isoprene, were selected due to their extremely low volatility and thus prone to deposit onto surfaces and condense onto aerosol particles.

590
The newly implemented model was applied to investigate the BVOCs exchange over a boreal forest canopy at SMEAR II (Station to Measure Ecosystem–Atmosphere Relations II) in Hyytiälä, Finland, in July 2010. The model set-up was the same as that in Zhou et al. (2017) except that the time period of July 2010 was simulated instead of August.

CONCLUSIONS

The measured and modelled diurnal patterns of fluxes at the canopy top are shown in Fig. 1. The measured fluxes of monoterpenes, isoprene+MBO, methanol, acetaldehyde and acetone show similar diurnal patterns which apparently follow the diurnal patterns of gas emissions. The upward fluxes are approximately zero during nighttime when the emission is low, while they increase after sunrise until about 16:00 in the afternoon reaching the maximum values. For methanol and acetaldehyde, the deposition also plays a significant role (Fig. 2). Hence, the fluxes can be downward at nighttime (Fig. 1c and 1d). The diurnal variations of fluxes for monoterpenes, isoprene+MBO, methanol and acetaldehyde are well represented by the model results. Although for isoprene+MBO the monthly-averaged daytime flux is underestimated by up to about 0.03 µg m$^{-2}$ s$^{-1}$ at around 17:00, the values are still in the range of measurement uncertainties. For acetone, the model underestimates the flux and shows a downward flux in the morning, indicating a possible overestimation of deposition effect. In contrast, the model shows a larger upward flux than measurement from about 10:00 to 16:00 at daytime, implying missing sources either from emission or chemical production. The monthly-averaged diurnal flux for formaldehyde is mostly downward and does not show an apparent diurnal pattern. The large uncertainties also indicate that although the deposition may play a significant role in its exchange processes, other effects, e.g. emission and chemical process, can still compete with deposition effect.

Figure 1: Measured (points) and modelled (line) monthly-averaged diurnal patterns of fluxes at the canopy top for (a) monoterpenes, (b) isoprene+MBO, (c) methanol, (d) acetaldehyde, (e) acetone, (f) formaldehyde. One standard deviation is shown for measurement data with error bars and modelled data with shaded area.
The model also provided a possibility to analyse individual sources and sinks within the canopy instead of only net fluxes at the canopy top for different compounds. The relative contributions of emission (Qemis), net chemical production and loss (Qchem), turbulent transport into the canopy (Qturb) and deposition onto vegetation and soil surfaces (Qdepo) are shown in Fig. 2. Here Qturb represents the in-canopy concentration change of BVOCs due to turbulent transport, which can be positive (downward) as a source term or negative (upward) as a sink term. For those compounds emitted from vegetation, e.g. isoprene and monoterpenes, Qemis is the dominant source. The chemical process is significant for highly reactive compounds, it can act as a net source for isoprene oxidation products ISOP34OOH and ISOP34NO3, and as net removal mechanism for sesquiterpenes. Deposition is the main sink for most compounds except monoterpenes, sesquiterpenes, isoprene+MBO. The emitted monoterpenes, isoprene+MBO inside the canopy are mainly lost via turbulent transport to the air above the canopy. The bidirectional flux above the canopy for methanol result from the competition between emission and deposition.

Figure 2: Modelled relative contributions of sources and sinks for different compounds within the canopy.

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FACTORISATION OF ORGANIC AND INORGANIC SPECIES IN AEROSOL MASS SPECTROMETRY

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Keywords: Aerosol mass spectrometry, factorisation, PMF

INTRODUCTION

Atmospheric particulate matter is a complex mixture of chemical species such as organic compounds, sulfates, nitrates, ammonia, chlorides, and refractory material. As aerosol chemical composition influences aerosol climate effects (via cloud condensation nucleus activation, hygroscopic properties, aerosol optics, volatility and condensation) as well as health effects (toxicity, carcinogenicity, particle morphology), detailed understanding of atmospheric fine particle composition is widely beneficial for understanding these interactions (McNeill, 2017).

METHODS

The comprehensive, detailed measurement of aerosol chemistry remains difficult due to the wide range of compounds present in the atmosphere as well as for the miniscule mass of the particles themselves compared to carrier gas.

Aerosol mass spectrometer (AMS; Jayne et al., 2000) is an instrument used for characterization of non-refractive aerosol types: the near-universal vaporization and ionisation technique allows for measurement of most atmospheric-relevant compounds. The downside of the hard ionisation applied is extensive fragmentation of sample molecules. However, the apparent loss of information in fragmentation can be partly offset by applying advanced statistical methods to extract information from the fragmentation patterns.

In aerosol mass spectrometry statistical analysis methods, such as positive matrix factorization (PMF; Paatero, 1999) is usually applied for aerosol organic component only, to (1) keep the number of factors to be resolved manageable, (2) to retain the inorganic components for solution validation via correlation analysis, and (3) to avoid inorganic species dominating the factor model. However, this practice smears out the interactions between organic and inorganic chemical components, and hinders the understanding of the connections between primary and secondary aerosols via atmospheric physicochemical processes (e.g. condensation and evaporation of gases) and on the other hand the potential non-linear summation of anthropogenic and biogenic aerosol emissions. From the perspective of statistical analysis there is no definite reason why inorganics could not be included, as long as their uncertainties are estimated correctly and their influence is properly weighted in the factor model. For result validation, external, additional information available from most measurement sites, such as correlations with trace gas concentrations or size distribution derived, mode-specific mass loadings can be used instead of AMS inorganics. In some promising recent analyses, inorganic species have already been added to PMF analyses and shown to interact with organic semi-volatile compounds (Sun et al., 2012).

RESULTS & DISCUSSION

We tested including all the default AMS chemical species, i.e. organics, sulfates, nitrates, ammonia and chlorides, in a PMF analysis, and present potential interpretations of the results with regard to aerosol sources and the chemical processes shaping the aerosol types. In addition to resolving organic-dominated aerosol classes, and comparing the result to the previous analyses (e.g. Äijälä et al., 2017), the results shed light on inorganic salt formation and may imply formation of organics salts.
From the preliminary factorizations performed, we observe ammonium nitrate and ammonium sulphate to contain most, but not all of nitrogen and sulphur of the aerosol. This observation points to the direction of organic salts as well as organic nitrogen and sulphur. We additionally observe factors related to amines, coal burning and traffic in many of the ambient data tested.

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