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OBJECTIVES AND THEIR UPDATES

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

Figure 1. Quantitative results of the GPP feedback loop obtained from observations made at SMEAR II, Finland, during 1996–2011. For each step, the percentage refers to the change in the second variable of that step that was related to the change in the first variable determined by the previous step. Figure from Kulmala et al. 2014b.
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.

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.

In the beginning of 2017, the UEF team will be strengthened by a new 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.

**SCIENTIFIC AND SOCIETAL SIGNIFICANCE OF THE COE ATM**

During the previous CoE periods, the Finnish atmospheric and Earth system science community has been systematically working towards building an internationally leading, integrated multidisciplinary research environment for atmospheric and Earth system science to study biosphere-aerosol-cloud-climate-air quality interactions. The key strength of our scientific approach is the combination of comprehensive, continuous long-term observations, extensive field and laboratory experiments, use of satellite data, and advanced modeling leading to theoretical understanding and quantitative predictions of different atmosphere-biosphere processes, and innovative method and instrument development. An important factor behind the success of the CoE ATM is the long-lasting, multidisciplinary collaboration between the Universities of Helsinki, University of Eastern Finland and FMI, and between the physics, chemistry and forest sciences within the UH. All PIs are experts in their research fields and contributing to the research, development of research methods and teaching for their topics.

As stated in the Scientific Advisory Board report: “The ATM CoE is a scientific endeavor that is ambitious, creative, and successful. It is recognized worldwide as the leading scholarly center for aerosol research and as one of the top centers for atmospheric science more broadly… Compared to previous periods the focus and number of groups have expanded and the CoE now spans a wide range of atmospheric science including observation based research on aerosol nucleation, growth and molecular composition, atmospheric chemistry. The CoE has solid contribution by biologists. It also includes observational elements focusing on the atmosphere - biosphere exchange of reactive species, greenhouse gases and energy. The observation based process studies are linked together through state-of-the-art modeling at a range of space and time scales. We note, that there are many institutes around the world with strong connections between atmospheric physics and atmospheric chemistry. Fewer have had the vision to push forward into the linkages to biology. The CoE is a pioneer in this respect.”

CoE ATM leader Markku Kulmala is the world leading scientist in the area of atmospheric nucleation and related biosphere-atmosphere interactions. Five of our researchers have been selected as Thomson Reuters Highly Cited Researchers 2014-2016: Markku Kulmala (UH), Douglas Worsnop (UH and UEF), Veli-Matti Kerminen (UH), Tuukka Petäjä (UH) and Ari Laaksonen (FMI). In addition, 13 of our researchers are among the 1000 most cited researchers in the field of geosciences including five younger scientists (post docs and tenure tracks). During the previous three years, we have received one ERC Advanced Research Grant, one
ERC consolidator grant, and two ERC Starting Grants, and two Academy professorships to the CoE ATM team, all signs of the outstanding scientific merits and excellence. We have also had two FiDiPro nominees and several international awards e.g. The Fedor P. Litke Gold Medal of the Russian Geographical Society, Distinguished Visiting Fellow status by IIASA, and two Chinese honorary professorships to Markku Kulmala, The 2015 Alfred Wegener Medal & Honorary Membership to Sergei Zilitinkevich, Fuchs Award to Douglas R. Worsnop, Nordic Aerosologist Award to Hanna Vehkamäki and International Aerosol Fellow Award 2016 to Kaarle Hämeri.

During the years 2014-2016 (June), the CoE ATM team has published 554 peer-reviewed scientific articles in high-level journals including 5 in Nature and 2 in Science. The work has produced several benchmarking studies regarding e.g. measurements and modeling on atmospheric new particle formation and gas-to-particle conversion processes (e.g. Kulmala et al. 2014a; Kürten et al. 2014; Ehn et al. 2014; Jokinen et al. 2015; Olenius et al. 2015; Kirkby et al. 2016; Tröstl et al. 2016; Bianchi et al. 2016; Lehtipalo et al. 2016; Sipilä et al. 2016; Duplissy et al. 2016; Merikanto et al. 2016), aerosol cloud interactions (e.g. Hansen et al., 2015; Pajunnoja et al., 2015; Väisänen et al., 2016), analysis of forest, peatland and lake ecosystem carbon and nitrogen budgets and related processes (e.g. Pumpanen et al. 2014; Mammarella et al. 2015; Köster et al. 2015; Petrescu et al. 2015; Stepanenko et al. 2016; Machacova et al. 2016), and development of sophisticated methods and models for atmospheric physics and chemistry (e.g. Steiner et al. 2014; Parshintsev et al. 2015; Franchin et al. 2015; Barreira et al. 2015; Wimmer et al. 2015; Kangaslouma et al. 2016). The preliminary quantitative answer to our main objective (COBACC feedback loop) is published by Kulmala et al. (2014b). Please see the research highlights in more detail in the next chapter.

In addition to scientific breakthroughs, we provide access to highly equipped field sites – like SMEAR II and Pallas-Sodankylä GAW, SMEAR IV in Kuopio for aerosol-cloud interaction studies, laboratories and unique datasets, as well as training and education for physics, forest sciences and chemistry. The joint and coherent experimentation and common method development will improve the repeatability of research results, maximize the benefits of running costly experiments, and make better use of the existing equipment, personnel and facilities.

The links from the scientific breakthroughs towards innovations are established via a close co-operation with SMEs, especially with two of our spin off companies providing aerosol particle counters, mass spectrometer products and ultrahigh sensitivity explosive trace detectors. Furthermore, FMI and UH have a strategic partnership with Vaisala Ltd and have close connections to other companies, e.g. Space System Finland. UH and FMI are partners in Cluster for Energy and Environment research consortium, CLEEN Ltd and contribute to the CLEEN research programs.

RESULT HIGHLIGHTS

During years 2014-2016, we have provided the first quantitative estimate regarding the ecosystem climate feedback (Kulmala et al. 2014b). This work is based on combining process-level understanding with comprehensive, long-term 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 and model simulations on the other hand. The importance of the continuous, comprehensive observations have been shown in addition to the feedback loop investigations, in the recent findings during solar eclipse (Jokinen et al. in review). The different findings at SMEAR stations have been also the basis for our leadership in the European Strategy Forum on Research Infrastructures (ESFRI) ICOS and ACTRIS.

Our research highlights from years 2014-2016 cover topics from atmospheric new particle formation, gas-to-particle conversion and cloud formation processes, to ecosystem processes, air quality, global climate, and development of new research methods. The atmospheric gas-to-particle conversion and new particle formation results include e.g. discovery of extremely low volatile organic compounds from monoterpenes.
oxidation forming a large source of secondary organic aerosols (SOA, Ehn et al. 2014, Kokkola et al. 2014),
discovery of pure biogenic nucleation without sulphuric acid (Kirkby et al. 2016), presenting a model using
combination of quantum chemistry and thermodynamics that can predict experimental sulphuric acid-water
particle formation (Duplissy et al. 2016; Merikanto et al. 2016), revealing the theoretical basis for first ever
molecular level understanding of atmospheric particle formation (Sipilä et al 2016), modelling work
showing that approximate continuum models for cluster and particle growth can lead to distortions of cluster
concentrations (Olenius et al. 2015), development of chemistry-aerosol-dynamic models to include a multi-
layer deposition module for all gaseous molecules (Zhou et al. 2016), development of new methods and
knowledge on particle counter operation, cluster generation and heterogeneous nucleation (Lehtipalo et al.
2014; Steiner et al. 2014; Kangasluoma et al. 2015, 2016; Franchin et al. 2015; Wimmer et al. 2015; Jokinen
et al. 2015; Wagner et al. 2016; Wang et al. 2016), observations of aerosol formation and concentrations at
various sites around the world (Paramonov et al. 2015; Nieminen et al. in preparation), and analysing long
aerosol and non-methane hydrocarbon (NMHC) data series from Arctic stations (Lihavainen et al. 2015;
Uttal et al. 2015; Hellén et al. 2015; Asmi et al. 2016; Anttila et al. 2016). The CLOUD studies have revealed
that e.g. biogenic SOA formation plays crucial roles in atmospheric cloud condensation nuclei production
(Dunne et al. submitted), that more hygroscopic particles are more prone scavenge into cloud droplets than
less hygroscopic particles (Väisänen et al. 2016), and increased our understanding of Arctic cloud layers
and their seasonality (Hirsikkko et al. 2014; Hirsikkko et al. in preparation). Also new methods have been
developed to verify the representation of microphysical processes in operational numerical weather
prediction models. In atmospheric chemistry, we have e.g. developed small scale on-line and off-line mass
spectrometry based method to study chemical reactions in gas phase (Duporté et al. 2016), and a novel
method based on comprehensive two-dimensional gas chromatography coupled to time-of-flight mass
spectrometry to determine vapor pressures of atmospheric aerosols (Parshintsev et al. 2014; Helin et al.
2015). In the ecosystem processes results, we have studied e.g. the effect of weather and needle ontogenesis
on monoterpane synthase activity, storage and emission in Scots pine (Vanhatalo et al. submitted),
monoterpane fluxes from forest floor (Mäki et al. 2016), and the effect of wind and water convection on the
surface exchange of carbon dioxide in lakes (Mammarella et al. 2015). It has been found that mature Scots
pine trees consistently emit N2O and CH4 (Machacova et al. 2016), and that wetland is a marked sink of
CO2 at subarctic Pallas supersite while spruce forest and alpine tundra has an annual balance close to zero
(Aurela et al. 2015), and that 137Cs has remained rather mobile in the forest soil for decades after Chernobyl
and Fukushima accidents, but the 137Cs in the structure of the trees remains (Pumpanen et al. 2016).

We have gained understanding on the feedback between atmospheric aerosol particles and the stability of
the boundary layer that limits the subsequent anthropogenic emissions to a shallower layer leading to
intensified poor air quality conditions in urban environments, particularly in China (Petäjä et al. 2016).
Ground and space based remote sensing instruments have been used to e.g. dramatically improve snow
observations (Metsämäki et al. 2015), to improve boundary layer analysis (Ding et al. 2016), to produce
frost/thaw mapping from satellite data for the northern hemisphere using L-band satellite radiometers that
is a totally new source of spatially reliable information (Rautiainen et al. 2014; 2016), and to show that air
with high aerosol content is associated with increased upper tropospheric humidity due to microphysical
effects of aerosols. Our Earth System Modelling approach has formed future scenarios for global
anthropogenic size-segregated particle number emissions (Paasonen et al. 2016), developed aerosol
formation modules for global models ECHAM-HAM and EC-Earth (Fang et al. 2015; Arneth et al. 2016),
investigated formation of extremely low volatile organic compounds and further cloud condensation nuclei
from biogenic emissions (Jokinen et al. 2015), developed methods for quantification of global dew
collection potential on artificial surfaces (Vuollekoski et al. 2015), and developed CarbonTracker Europe-
CH4 to estimate global methane emission (Tsuruta et al. 2015). Joint activities with the various research
groups within the CoE ATM enable us to study the chains of chemical reactions and physical processes that
secondary pollutants, such as ozone and organic aerosols, undergo in China's polluted urban air (Kulmala
2015), and enable us to study atmospheric vapor, cluster and nanoparticle concentrations, dynamics, and
their connection to atmospheric nucleation (Kulmala et al. 2014a).
KEY PUBLICATIONS


*Reasoning:* This paper provides the first quantitative estimate regarding terrestrial climate feedback combining process-level understanding with comprehensive, long-term field measurement data set collected from a boreal forest site SMEAR II. Our estimate of the gain in GPP resulting from the feedback is 1.3, which is larger than the gains of the few atmospheric chemistry-climate feedbacks estimated using large scale models. Our analysis demonstrates the power of using long-term, 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.


*Reasoning:* In this Nature paper, the extremely low volatile organic compounds (ELVOC) are found from the first time from monoterpene oxidation forming a large source of secondary organic aerosol, and also for atmospheric new particle formation.


*Reasoning:* This paper belongs to the series of four papers that were published in Nature, Science and Nature Communications in May 2016 presenting results from nano-particle growth in the CLOUD (Cosmics Leaving OUtdoors Droplets) chamber. The paper gives new knowledge on the growth of freshly formed aerosol particles that is crucial in their survival to cloud condensation nuclei. It was found that atmospheric ions and small acid-base clusters can enhance the growth process, and that the availability of compounds capable of stabilizing sulphuric acid clusters governs the magnitude of these effects.


*Reasoning:* This paper is a good example of the tight link between the forest sciences and atmospheric research within our CoE ATM. It is shown that emissions of biogenic volatile organic compounds (BVOC) by boreal evergreen trees have strong seasonality, with low emission rates during photosynthetically inactive winter and increasing rates towards summer. High emission peaks caused by enhanced monoterpene
synthesis were found in spring periods simultaneously with photosynthetic spring recovery. This suggests that these emissions may serve a protective functional role for the foliage during this critical transitory state and that these high emission peaks may contribute to atmospheric chemistry in the boreal forest in springtime.


Reasoning: This Nature comment by the ATM CoE leader represents our efforts to understand the chains of chemical reactions and physical processes that secondary pollutants, such as ozone and organic aerosols, undergo in China’s polluted urban air. Results are hard to predict because many physical and chemical processes — such as surface chemistry, oxidation, clustering and dynamical effects — happen simultaneously. We need a holistic solution. The paper includes also the roadmap how to solve the challenging air quality problem.

RESEARCH INFRASTRUCTURES AND COLLABORATION

CoE ATM is the main user of INAR RI infrastructure together with the Tampere University of Technology, CSC IT Center for Sciences, and Natural Research Institute. INAR RI belongs to the Finnish RI roadmap 2014-2020, and integrates the national leading organizations and infrastructures in the atmosphere-ecosystem research. In the core of INAR RI is the continuous, long-term field observations via national network of SMEAR (Station for Measuring Ecosystem Atmosphere Relationships) stations combined with laboratory measurements and modelling. New cooperation regarding Finnish ecosystem research and its linkages to atmospheric sciences is starting with the Universities of Oulu, Turku and Jyväskylä, and Finnish Environment Institute through INAR RI Ecosystems concept. INAR RI Ecosystems will provide extended understanding on the functioning of forest, peatland, agricultural, urban and lake ecosystems, and their interactions with the atmosphere.

The CoE ATM community is leading two ESFRIs (European Strategy Forum on Research Infrastructures) with their head offices in Finland at Kumpula Campus: ICOS (Integrated Carbon Observation System) and ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network). CoE ATM also has an active role in ESFRIs ANAEE (Infrastructure for Analysis and Experimentation on Ecosystems) and eLTER (European Long-Term Ecosystem Research). The environmental research infrastructure field in Europe is very fragmented, and therefore coherent and coordinated operations of different ecosystem and atmospheric RIs are urgently needed. CoE ATM has a coherent, co-located and operational infrastructure combining measurements on atmospheric processes, greenhouse gases and ecosystem functioning, and is thus a forerunner in the implementation of environmental and biological RIs in Europe. We have also taken the first steps towards building a global network of SMEAR stations to strengthen the coverage of global climate data and thus improve the accuracy of climate observations and future scenarios.

Other international research infrastructures that we actively use are e.g. CLOUD chamber at CERN, Welgegund measurement station in South Africa, SMEAR Estonia, SORPES Nanjing, China and Tiksi, Russia.

The CoE ATM is active in national and international collaboration. We collaborate with all relevant national organizations including e.g. Tampere University of Technology, Lappeenranta University of Technology, CSC IT Center for Sciences, and Natural Research Institute Finland through various research and research infrastructure projects. New cooperation regarding ecosystem research infrastructure integration has been initiated with Universities of Oulu, Turku and Jyväskylä, and Finnish Environment Institute. The extent of our international collaboration is vast and covers cooperation in research, research infrastructures, education and innovations in Nordic, European and Global level. CoE ATM community has essential role in two ESFRI’s with their head offices in Finland at Kumpula Campus: ICOS (Integrated Carbon Observation System) and ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network). CoE ATM
also has an active role in AnaEE ESFRI (Infrastructure for Analysis and Experimentation on Ecosystems) and in the emerging ESFRI LTER (Long-term Ecosystem Research network). In addition, CoE ATM is actively involved and contributes data to various international Earth observation systems and networks as well as FP7 and H2020 projects (e.g. LifeWatch, SIOS, InGOS, WMO-GAW, EMEP, Interact, FluxNet, AERONET, SOL-RAD-NET, EARLINET, EXPEER). We also enhance the international leadership of Finnish researchers in atmosphere and terrestrial research via new initiatives PEEX (Pan Eurasian Experiment, www.atm.helsinki.fi/peex/) and Beautiful China that have the focus in the boreal and arctic climate regions.

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ECOSYSTEM PROCESSES – Activities in 2015-16


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2Dept. of Physics, University of Helsinki, Finland
3Dept. of Environmental and Biological Sciences, University of Eastern Finland, Kuopio, Finland
4Dept. of Food and Environmental Sciences, University of Helsinki, Finland
5Dept. of Environmental Sciences, University of Helsinki, Finland
6Dept. of Chemistry, University of Helsinki, Finland
7ICOS ERIC, Helsinki, Finland
8Global Change Research Institute CAS, Brno, Czech Republic

The Ecosystem processes –team in the ATM Center of Excellence has in 2015-16 been implementing the research plan and produced several important findings, highlighted in the FCoE Abstract Book. Most of the activities link to other themes as well, thus only a brief summary is presented here.

Our 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 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 four themes: Exchange of aerosol precursors between ecosystems and atmosphere, Whole tree physiology, Optics of photosynthesis, and Biogeochemical cycles and element budgets.

1. EXCHANGE OF AEROSOL PRECURSORS BETWEEN ECOSYSTEMS AND ATMOSPHERE

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.

**Seasonal variation in monoterpane emission capacity of Scots pine (Aalto et al)**

We have utilised the long-term measurements of VOC emissions at shoot and ecosystem scales to quantify and analyse the driving factors behind the fluxes in boreal ecosystems. It seems evident that applying constant emission capacity in VOC emission modeling will likely result in significant, season-related biases in emission estimates (Aalto et al 2015). The needle age classes clearly differ both in emission potentials and in features related to seasonality (Aalto et al 2014). If these features are not taken into account in modeling the production of precursors for atmospheric secondary aerosol formation, it will likely lead to significantly biased results.

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

**Understory measurements of biogenic volatile organic compounds by solid-phase microextraction and portable gas chromatography-mass spectrometry (Barreira et al)**

Boreal forest soil and understorey vegetation contributes to the ecosystem scale fluxes by emitting or adsorbing diverse range of volatile organic compounds. Therefore the accurate quantification of unknown VOC sources, including soil, can improve air chemistry models and potentially also reveal currently missing OH sinks. The soil processes affect the below-canopy fluxes of VOCs, and we have quantified the exchange using novel analytical methods and experimental approaches.

The measurements were carried out with three semi-automated chambers connected to the proton-transfer reaction mass-spectrometer (PTR-MS) during the snow-free period from 2010 to 2015 (Mäki et al this issue). The results showed that the forest floor VOC exchange was dominated by monoterpenes, methanol, and acetone. The seasonal dynamics of monoterpane emissions was closely correlating with the monoterpane-rich litter input from the canopy, and the highest monoterpane fluxes were measured in the spring and fall.

Solid-phase microextraction (SPME) combined with portable gas chromatography-mass spectrometry was successfully applied to on-field measurements of atmospheric BVOCs in soil chambers and ambient air (Barreira et al: this issue). Among the atmospherically relevant monoterpenes and aldehydes, α-pinene and Δ²-carene were the most abundant BVOCs. The quantities of monoterpenes measured from soil chambers simultaneously by portable GC-MS and monoterpane fluxes measured by PTR-MS were in close agreement. The ambient BVOC amounts were significantly higher when wind direction was from South-East, as a consequence of transportation of these compounds from the nearby sawmills.

**Terpenoid, acetone and aldehyde emissions from Norway spruce (Hakola et al)**

Previously we have been quantifying the Scots pine emissions in our field station in great detail, but Norway spruce, although a very important tree in boreal forests, has been much less studied. The spruce volatile organic compounds (VOC) emissions were measured in campaigns in 2011, 2014 and 2015 (Hakola et al this issue) over altogether 14 weeks in spring and summer. The measured compounds included isoprene, monoterpenes (MT), and sesquiterpenes (SQT) and in 2015 also acetone and C₄-C₁₀ aldehydes. MT and SQT emission rates were low during spring
and early summer. MT emission rates increased to their maximum at the end of June and the MT emission pattern varied a lot from tree to tree. A significant change in SQT emissions took place at the end of July. In August SQT were the most abundant group in the emission, β-farnesene being the most abundant compound. SQT emissions increased simultaneously with linalool emissions and these emissions were suggested to be initiated due to some stress effects. Acetone and aldehyde emissions were highest in July, when they were approximately at the same level as MT.

**How a pathogenic fungus breaks tree resistance? (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 wide-spread 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. Preliminary results show that *E. polonica* infection decreases both water surface tension and stem hydraulic conductance. Further experiments will reveal the consequences on tree VOC production mechanisms and their consequences to atmospheric processes.

**Role of needle surface waxes in dynamic exchange of mono- and sesquiterpenes (Joensuu, et al)**

The different physicochemical properties of BVOCs affect their transport within and out of the plant as well as their reactions along the way. Some of these compounds may accumulate in or on the waxy surface layer of conifer needles and participate in chemical reactions on or near the foliage surface. We determined whether terpenes, a key category of BVOCs produced by trees, can be found on the epicuticles of Scots pine (*Pinus sylvestris* L.) and, if so, how they compared with the terpenes found in shoot emissions of the same tree (Joensuu et al 2016). We measured shoot-level emissions of pine seedlings at a remote outdoor location in central Finland and subsequently analysed the needle surface waxes for the same compounds. Both emissions and wax extracts were clearly dominated by monoterpenes, but the proportion of sesquiterpenes was higher in the wax extracts. There were also differences in the terpene spectra of the emissions and the wax extracts. The results, therefore, supported the existence of BVOCs associated to the epicuticular waxes.

**Free amino acids in atmospheric aerosols in boreal forest (Helin et al)**

Primary biological aerosol particles (PBAPs) are emitted to the atmosphere from vegetation and other living organisms. Their importance to atmospheric chemistry and physics has increased
interest towards their reliable determination. Traditionally, living organisms have been studied in particles with cultivation (highly specific) or by microscopy (light or fluorescence). However, molecular genetic analysis techniques are nowadays most frequently used, since they provide information not only about viable cell, but also on uncultivable or dead cells or on plant or animal fragments. Another approach to determine particles of biological origin is based on chemical tracer techniques. The clear advantage of chemical tracers, that are not limited only to amino acids, carbohydrates, proteins and peptides, and rarely lipids, is the possibility for quantitative analysis, while the main disadvantage is disability to identify different biological species. The aim of this study was to determine the FAAs concentrations in atmospheric aerosol samples collected in boreal forest. Different particle size fractions were collected throughout the year in order to determine the annual variation and to identify possible sources. The samples were analyzed by using hydrophilic interaction liquid chromatography combined with triple quadrupole mass spectrometer operated in multiple reaction monitoring mode. The obtained FAA data was compared to previous results, where the abundance of bacteria and fungi were characterized and the total DNA concentration in aerosol particles given.

The total concentrations of FAAs in the aerosol filters had a distinct seasonal variation being the most abundant in late spring and early summer, and during autumn. Furthermore, some trends in the amino acid distributions in different size fractions in aerosol filters were observed. These detected variations agree with our previous studies.

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.

Linking stem growth respiration to the seasonal course of stem growth and GPP of Scots pine (Chan et al)

An in-depth analysis of in situ stem growth and growth respiration dynamics demands was made. Stem volumetric growth and growth respiration and GPP were intimately linked to each other. The ratio of volumetric growth rate and growth respiration varied systematically in different stages of growth., i.e.it was different amongst phases of cell division, cell wall enlargement and cell wall thickening, A large focus on tree cellular respiration at specific developmental stages, its linkages to source-sink processes and environmental drivers, and a robust method to calculate woody tissue costs also require further investigation.

Belowground hydraulic conductance calculated from simultaneous sap flow and xylem diameter change measurements in mature Scots pine trees during springtime (Hölttä et al)

A combination of sap flow and xylem diameter change measurements was used to calculate belowground hydraulic conductance. Belowground hydraulic conductance was a strong function
of soil temperature during spring 2013. The method and results seem promising and data from more trees and more years will be analyzed in the future.

**Stomatal and non-stomatal limitation of photosynthesis (Salmon et al)**

Combined laboratory and field experiment show that stomatal limitation of photosynthesis dominate under normal tree physiological conditions although also non-stomatal limitations were evident. However, under extreme stress, non-stomatal limitation become dominant. Furthermore, the non-stomatal limitation of photosynthesis seems to be obey the same rule across species.

**Temperature based mechanistic model of winter-time diameter changes in three tree species reveals differences in stem elasticity and in plasma membrane water permeability (Lindfors et al)**

Freezing is lethal to living cells, but the perennial plants have many ways to avoid intracellular freezing. We showed quantitative evidence how stem and xylem diameter changes can be used to study extracellular freezing. Diameter changes of frozen xylem and phloem can be predicted using temperature. Permeability of plasma membrane and elasticity of xylem and phloem was estimated for 3 tree species using diameter change measurements. Temperature hysteresis was detected in permeability of plasma membrane.

**Low plant water status decreases the ice nucleation temperature of trees (Lintunen et al.)**

We study the linkage of xylem water status with apoplastic ice nucleation temperature and with the size and duration of a freezing exotherm. We have found that relative tissue water content and apoplastic ice nucleation temperature are significantly higher for angiosperms than for gymnosperms both in winter and in spring, and the difference in ice nucleation temperature disappears when the branches are saturated with water. Ice nucleation temperature is not correlated with the size of a freezing exotherm, but it is correlated with the duration of an exotherm, i.e. the lower the freezing temperature, the faster the freezing propagation. This has implications to the risk of winter embolism formation in trees via the size of gas bubbles formed in the ice.

**Optimal stomatal conductance in coupled steady-state photosynthesis models solved analytically by approximation (Mauranen et al)**

A steady-state photosynthesis model for trees that couples water transport (xylem and evapotranspiration) and carbon absorption (phloem and photosynthesis) was developed. Control of stomatal opening was assumed to be a means for the plant to maximize its metabolic rate. Photosynthesis rate, which in this steady-state model represents also a more general metabolic rate, was formulated as a non-linear function of carbon dioxide concentration of the air inside the leaf. Two different formulations were tried for the function, and both resulted in a model that was solvable analytically using reasonable approximations. The resulting formulae for optimal stomatal conductance qualitatively agree with observed phenomena and give new interpretations to empirical constants in previous theoretical work.
The role of SLAC1-mediated rapid stomatal closure in the ecophysiology of plants (Ehonen et al)

Populus species seem to have lost the functional features of SLAC1 anion channels that is essential for the rapid closure of stomata. We have made transgenic hybrid aspen trees where we have introduced the Arabidopsis SLAC1 channel in order to rescue the mechanism. A long term field experiment started this autumn with the transgenic hybrid aspen lines.

A combination of source and sink effects determine growth of Scots pine organs in different environmental conditions (Schiestl-Aalto et al)

Whether growth is limited by sink strength (driven by environmental factors such as temperature, water and nutrients) or source (photosynthetised or stored carbon) is under discussion. We constructed a model to test the factors that limit growth at different time scales. A combination of source and sink effects (temperature and GPP) was needed to produce realistic intra- and inter-annual variation to modelled growth of shoots, needles and secondary growth. With direct and indirect temperature effects intra-annual growth variation was modelled successfully but GPP effects at different temporal scales were needed for the description of inter-annual variation.

3. OPTICS OF PHOTOSYNTHESIS

In the Optics of photosynthesis Lab we study the dynamics of plant eco-physiological processes using optical data, and develop new methods to measure and interpret it. We combine measurements at the leaf and canopy level, lab experiments and long-term field data acquisitions, and process-based model development and validation. Our key goal is to develop new mechanistic understanding and optical tools to facilitate the study of vegetation processes from contact measurements, towers, airborne platforms and satellites.

Upscaling chlorophyll fluorescence from the forest to the satellite pixel (Atherton et al)

The retrieval of solar-induced chlorophyll fluorescence (SIF) from space promises to deliver new insights into gross primary productivity (GPP). Recently, strong empirical relationships have been observed between SIF and GPP for the boreal forest region. In this study we aim to uncover the functional mechanisms that relate space measurements of SIF to boreal forest GPP. We do this by validating SIF retrievals from GOME-2 with field observations from SMEARII research station. Field observations include GPP, as measured by the eddy covariance technique, and the leaf level yield of chlorophyll fluorescence (\(\phi_f\)) measured using a MONIPAM system. SIF generally tracks canopy level GPP, but diverges from \(\phi_f\). This is partly explained by the dependence of SIF on absorbed photosynthetically active radiation, but there may also be other mechanisms, such as under-story fluorescence, contributing to the divergence.

Seasonal changes in leaf fluorescence spectra: controls and implications (Porcar-Castell et al)

Chlorophyll fluorescence is being measured from space at different wavelengths and used as a proxy to track seasonal dynamics in vegetation photosynthesis. We examined the seasonal variation in leaf-level fluorescence spectral properties, characterized the controls, and discuss the impact of this variation in the interpretation of fluorescence data. We found out that the fluorescence spectra is not constant as a result of changes in photosystem structure and possibly
stoichiometry but suggest that this variation will have small impact of the interpretation of satellite data.

4. BIOGEOCHEMICAL CYCLES 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.

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

We measured ecosystem scale CO₂ fluxes in 2012-2015 and found the stand to be a sink of carbon. The sink strength was the highest on the warmest and sunniest growing season and the lowest in the chilliest year. TER and GPP showed a strong, positive correlation with temperature sum calculated until the end of August. The observed variation in growth did not respond to the variation in annual GPP or NEE. Next the understanding of carbon balance of Scots pines will be deepened by a detailed study on root actions in the framework of a whole treewith measurements in SMEAR I and SMEAR II.

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.

Climate change induced pH decrease in the sensitive lake ecosystems – “ocean acidification” in lakes (Rantakari et al)

The release of carbon dioxide (CO₂) from anthropogenic sources has increased the atmospheric CO₂ concentrations. Oceans have absorbed about 30% of these emissions. However, when CO₂ is absorbed by seawater, the dissolved CO₂ induce chemical reactions that reduce seawater pH. This ocean acidification has been shown to seriously affect marine wild life. So far, no reports of the effects of increasing atmospheric CO₂ on pH of lakes have been published. We studied pH
changes in acid sensitive lakes in Finland between 1984 and 2005. The actual study period was chosen to be the latest 15 years prior to present, i.e. 2000-2015, because previously anthropogenic acid deposition caused by sulfur and nitrogen affected these lakes. As a reference, we also studied the 15 year period prior the actual study period i.e. 1984-1999. We used Mann-Kendall test to identify the trends in lake water pH during the study period. We found that all of the studied lakes showed recovery from previous anthropogenic acidification indicated by increasing pH in 1984-1999. However by 2015 in 9 lakes increasing trend in pH had turned into a decreasing trend, and furthermore, in 3 lakes an increasing trend in pH had levelled showing no significant trend between 2000 and 2015. These are the first results showing that increasing atmospheric CO₂ will decrease pH also in lakes, not only in oceans.

**Seasonal courses of methane fluxes in boreal trees (Machacova et al)**

Recent studies have shown that plants can significantly contribute to the CH₄ exchange between ecosystems and the atmosphere, but investigations on trees, particularly boreal tree species, are still rare. Seasonal CH₄ fluxes from stems of common boreal tree species – Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*) and downy and silver birch (*Betula pubescens, B. pendula*) – and the forest floor, were determined. Our results show that mature boreal trees exchange CH₄ with the atmosphere throughout the whole year with minimum and maximum fluxes during dormant and vegetation period, respectively, and the fluxes are modulated by soil water content. The tree species studied emitted CH₄ mainly during the vegetation season, however, considerable emissions were detected already from February onwards. The stem CH₄ emissions of trees may reduce the sink strength of soils in boreal forests.

**Spring recovery and variation in methane fluxes from boreal trees in southern Finland (Haikarainen et al)**

Trees are noted to be capable of transport microbially produced methane (CH₄) from anaerobic soil conditions to the atmosphere. We measured the variation in tree CH₄ flux during the spring 2015 from stems and shoots of downy birches (*Betula pubescens*) and Norway spruces (*Picea abies*) in Hyytiälä. Methane was emitted from stems and shoots of both tree species, and emissions were generally higher from birches than from spruces. Methane emission rates from birches correlated positively with soil temperature and also increased as the growing season proceeded. Trees living in the boreal region are capable to emit CH₄, but there is still some unidentified temporal and spatial variation in CH₄ between species.

**Comparison of the above canopy and the forest floor methane flux modelled by soil water content (Halmeenmäki et al)**

The upland soils have a capacity to emit CH₄, when soil moisture is at adequate level, and also vegetation has been found to contribute to the ecosystem-atmosphere CH₄ exchange. The sources and the mechanisms of the observed CH₄ emissions from the forests are still mostly unknown. By utilising lidar data and in situ measurements of CH₄ fluxes and soil moisture, we have modeled the potential CH₄ flux of a boreal forest floor. The potential forest floor CH₄ flux will be compared to the measured above canopy CH₄ flux.

**₁³⁷Cs distributions in soil and trees in forest ecosystems after the radioactive fallout – comparison study between Southern Finland and Fukushima, Japan (Pumpanen et al)**
The nuclear accidents in Chernobyl and Fukushima released large amounts of $^{137}$Cs radionuclides into the atmosphere that spread over large forest areas, and their distribution and fate in forest ecosystems is of importance due to their slow decay rate and possible accumulation in forest products. We compared the $^{137}$Cs concentration distribution in different parts of two coniferous forest ecosystems (needle litter, stems and at different depths in the soil) over short and long term in Finland and Japan (Pumpanen et al 2016). We also estimated the time needed to reach steady-state $^{137}$Cs activities after the $^{137}$Cs fallout in different parts of the ecosystem based on a 27-year-long dataset collected in Southern Finland. $^{137}$Cs distributions after two nuclear accidents occurred in Fukushima in 2011 and in Chernobyl in 1986 were compared between two coniferous forest ecosystems in Finland and Japan. The vertical distributions of $^{137}$Cs originating from the nuclear accidents were similar in Finnish and Japanese forests. The $^{137}$Cs was still mobile in the soil surface layers 27 years after the accident and it remains in the internal cycle of the forest ecosystem for decades.

**Role of tannins in carbon and nitrogen cycling of boreal forest soil (Adamczyk et al)**

To predict long-term soil C storage and climate feedbacks, we need profound understanding of dynamics and drivers of SOM decomposition. The aim of the study was to show how mycorrhizal plants affects SOM decomposition in polyphenolic-rich ecosystem. We measured different N pools, activities of organic matter degradation related enzymes and content of tannins (acid-butanol assay) as well as nitrogen pools including inorganic N (ammonium and nitrate), total free amino acids, degradable and recalcitrant N (acid hydrolysis) from humus mesh bags that were buried in boreal forest soil for one to three years. The results suggests that mycorrhizal plants build up recalcitrant SOM using root-derived tannins. We propose that turnover rate of plant roots with high CT content is crucial for SOM quality and quantity.

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

Forests are central as renewable natural resources and as sources for many immaterial goods as well. The management and use of forests in EU has large impacts not only on the economy but also on the EU responses to global grand challenges such as climate change and biodiversity conservation. The 2015 Paris Agreement of the UNFCCC, Convention on Biological Diversity and the following EU regulations acknowledge the need for sustainable forest management. This in turn requires detailed knowledge on how forests and their management may contribute to biodiversity, carbon capture and storage. Science has shown this to be a complex issue where policymakers require scientific advice on the potential trade-offs, synergies and conflicts. This presentation will highlight the current scientific understanding on climate impacts of European forests, their role in biodiversity conservation, and the potential for climate change mitigation through forest management, where current and planned policy tools have important role. There are different well-designed management options, with which the climate mitigation impact of European forests can potentially be enlarged, taking into account the local conditions, (new) wood based products and energy, land use history and forecasted changes in factors influencing forest vitality and productivity. These include e.g. the choice of tree species, planting density, fertilization, modifications in rotation length and timing of harvesting activities.
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Ehonen, S., J. Vahala, T. Hölttä, E. Nikinmaa, J. Kangasjärvi (this issue): The role of SLAC1-mediated rapid stomatal closure in the ecophysiology of plants
Haikarainen, I., E. Halmeenmäki, K. Machacova, M. Pihlatie (this issue): Spring recovery and variation in methane fluxes from boreal trees in southern Finland
Halmeenmäki, E., I. Haikarainen, O. Peltola, M. Pihlatie (this issue): Comparison of the above canopy and the forest floor methane flux modelled by soil water content


Kulmala, L., S. Dengan, P. Kolari, J. Bäck, F. Berninger, A. Vanhatalo, L. Matkala, T. Vesala, P. Hari, J. Pumpen (this issue): Four years of CO₂ exchange measurements reveal that the ecosystem scale fluxes are strongly temperature-limited in a subarctic Scots pine stand, SMEARI

Lindfors, L., J. Atherton, T. Hölttä (this issue): Temperature based mechanistic model of winter-time diameter changes in three tree species reveals differences in stem elasticity and in plasma membrane water permeability

Lintunen A., et al. (this issue): Low plant water status decreases the ice nucleation temperature of trees


Machacova, K., E. Halmeenmäki, M. Pihlatie, O. Urban (this issue): Seasonal courses of methane fluxes in boreal trees.


Schiestl-Aalto, P., L. Kulmala, A. Mäkelä (this issue): A combination of source and sink effects determine growth of Scots pine organs in different environmental conditions.
Summary on the activities of the aerosols and ions group during year 2016


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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 from boreal forest in Hyytiälä to Amazonian rainforest and is also active in instrument development. The aims of AIGG are to measure and understand 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 with brief outlook on the future.

ATMOSPHERIC MEASUREMENTS

Research conducted by AIGG members, in close collaboration with other research groups, led to several distinctive publications: a report from a mountaintop campaign, series of flight campaigns and understanding of atmospheric NPF based on long term particle and ion size distribution measurements. Bianchi et al. (2016) reported observations on new particle formation in the free troposphere from a campaign conducted at the Jungfraujoch high-altitude measurement station (3466 m a.s.l.) in Switzerland. Their main finding was that the neutral nucleation pathway dominated the NPF process, but was restricted to short time periods when the planetary boundary layer meets the free troposphere air masses. Väänänen et al. (2016) combined data from total of 111 flight hours to study the spatial and vertical extend of NPF around Hyytiälä measurement station. Their data showed NPF in the free troposphere, and that the ground and flight data were in good agreement in the boundary layer. Leino et al. (2016) analysed 10 years of ion data from Hyytiälä to show that the presence of intermediate ions (2-7 nm) is a useful indicator of NPF, while Mazon et al. (2016) concentrated on night-time cluster events and their connection to daytime ion formation. Kontkanen et al. (2016) published results from the PEGASOS campaign conducted in Po-valley, Italy, and found very high concentrations of sub-3 nm particles.

LABORATORY EXPERIMENTS

AIGG is participating in the CLOUD chamber experiments at CERN. This year the efforts of the project resulted in four high level publications. Kirkby et al. (2016) showed NPF to happen also with biogenic precursors only, which can be an important NPF mechanism in pristine areas with low sulfur pollution. Ion-induced nucleation was found to produce particles with rates one order of magnitude higher than only neutral particle production. While this study focused on the NPF, Trostl et al. (2016) analysed the role of the organic vapors on the particle growth in the sizes from 1 to 10 nm. Their data explain the early growth of particles with the very low volatility compounds, and the accelerated growth with increasing size with decreased particle curvature and condensation of also higher volatility compounds. The results were quantitatively modelled, and the authors present that the effect to the parametrized nucleation rates can be up to 50%. Lehtipalo et al. (2016) studied the importance of acid-base clustering on the sulfuric acid driven growth, which leads to enhanced growth rates compared to pure sulfuric acid growth. The fourth publication is by Duplissy et al. (2016), who examined binary sulfuric acid/water nucleation at various temperatures, relative humidities, sulfuric acid and ion concentrations. The data set was compared to a model from a companion paper (Merikanto et al. 2016), exhibiting excellent agreement.
The role of electric charge in heterogeneous nucleation on seed particles has not been unambiguously explored until now, when Kangasluoma et al. (2016c) showed that in fact the chemical composition of the seed particles plays a more important role than the charge during heterogeneous nucleation on sub 3 nm seeds. Visiting PhD student Yang Wang from the group of Prof. Biswas (Washington University in St. Louis) studied the ion and particle formation in pure and doped flames, showing the effect of dopant on the particle density (Wang et al. 2016).

INSTRUMENT DEVELOPMENT

This year AIGG published two instrument guideline papers and three instrument characterization papers. Manninen et al. (2016) gives extensive guidelines on the operation of the Airel neutral and ion air spectrometers (NAIS), while Kangasluoma et al. (2016b) showed the performance of the Airmodus particle size magnifier at various inlet pressures and temperatures, and presented a design for an inlet system, which minimizes the sampling losses. The ion measurement mode of the NAIS was characterized by Wagner et al. (2016), who found that the measured ion concentrations were underestimated at sizes below approximately 15 nm. Kangasluoma et al. (2016a) performed a characterization for the high resolution Herrmann type differential mobility analyzer, which is a frequently used ion mobility classifier in our aerosol laboratory. Franchin et al. (2016) developed and characterized a new high transmission inlet for the Caltech nano radial DMA, improving the nanoparticle size distribution measurements below 10 nm size.

CONCLUSIONS AND FUTURE OUTLOOK

The previous year was successful for the AIGG in terms of experiments and publications. Still on-going analysis is related to a successful campaign in Siikaneva peatland site, first sub-3 nm cleanroom ultrafine particle data set, understanding the connection of roll vortices to NFP in the boundary layer, finding out if and when nucleation happens in Amazonas and work toward optical closure of particle properties. Future efforts include new experiments in the CLOUD chamber and an indoor measurement campaign at Hartwall ice hockey arena. Several new instrument development projects were started concentrating on the sub 10 nm particle sizing and fast counting and the group was hosting a prototype CPC workshop during the summer 2016.

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![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, $A_{tot}$ and $V_{tot}$ are the total aerosol surface area and volume concentrations, respectively, CCN refers to cloud condensation nuclei, and CDNC is the cloud droplet number concentration.](image)

The effect of aerosols on gross primary production (GPP) has so far been analyzed only in terms of clear-sky conditions and thus by considering the effect of radiation scattering by aerosols, as demonstrated in
the upper branch of the COBACC feedback mechanism. Recently, Paasonen et al. (abstract in this
collection) have started analyzing how the cloud cover affects GPP, thus combining the COBACC
branches to a third, positive feedback mechanism. In this mechanism the increased cloud droplet number
concentration decreases the radiative transmittance of the atmosphere, which leads to a reduced GPP and
decreased amount of CO$_2$ captured by the ecosystem. In order to quantify this long-term feedback (related
to the lifetime of CO$_2$) arising from short-lived climate forcers, further calculations are planned for
estimating the changes e.g. in ecosystem respiration due to long-term changes in GPP.

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 summarize the current status of this work.

ADVANCES IN UNDERSTANDING AND HIGHLIGHTS OF THE RESULTS

Biogenic volatile organic compounds: emissions, concentrations and chemistry

Volatile organic compounds (VOCs) originating from bio- or anthropogenic sources play a significant role
in atmospheric chemistry and physics. Based on data obtained from long-terms measurements at the
SMEAR II station in Hyytiälä, Kontkanen et al. (2016a) developed proxies for the concentrations of
monoterpenes and their oxidation products. These proxies take into account temperature-controlled
emissions from the forest ecosystem, dilution caused by the mixing within the boundary layer and
different oxidation processes. All versions of the proxies capture the seasonal variation of the
monoterpene concentration.

Initial steps of atmospheric new particle formation

The work in this subject area aims toward improved understanding of atmospheric nucleation
mechanisms. Kontkanen et al. (abstract in this collection and submitted manuscript) compared
concentrations of sub-3 nm atmospheric particles measured with a PSM at 9 sites 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.

Ions have long been though to participate in the early steps of atmospheric new particle formation, yet
their exact role in this process has remained ambiguous. Chen et al. (2016) investigated the connection
between ionizing radiation and air ions at SMEAR II based on long-term measurements. The study
showed a clear effect of ionising radiation on air ion production and found some evidence on a connection
between the ionising capacity and cluster ion concentrations in the lower atmosphere. Chen et al. (abstract
in this collection) has investigated theoretically the relationship between the ionising radiation and air
ions. This latter work is currently in progress.

Buenrostro-Mazon et al. (2016) investigated the formation of charged clusters and their growth, termed
ion events, based on long-term observations at the SMEAR II station. The analysis showed that ion events
are frequent during both night and daytime. Nighttime ion events tend to occur before mid-night and the
formed ions rarely grow into sizes larger than 3-4 nm. Daytime ion events are associated strongly with
atmospheric new particle formation and, in comparison to nighttime ion events, a bigger fraction of the
ions reach sizes $>$2-3 nm.

Atmospheric new particle formation and growth
In this subject area, we have been involved in field observations and related theoretical studies. Dada et al. (abstract in this collection) combined 20 years of observations of atmospheric new particle formation (NPF) at the SMEAR II station. The analysis investigated first the effect of cloudiness on NPF and then compared the NPF event and non-event days under clear-sky conditions. As expected, the frequency of NPF events was found to be higher under clear-sky conditions compared with cloudy conditions. By focusing on clear-sky conditions, clear differences in many variables related to NPF were observed between the event and non-event days. For spring time, a threshold values for the ambient temperature and condensation sink (CS) were found, above which practically no clear-sky NPF event could be observed.

Kulmala et al. (2016) summarized the recent work on NPF taking place in Chinese megacities. It was shown that NPF occurs more frequently than what would be expected based on our current theoretical understanding on atmospheric NPF under heavily-polluted conditions that are common in these environments. This observation is a clear indication of yet unknown chemical reactions or NPF pathways specific for heavily polluted conditions.

Identifying atmospheric NPF events from the aerosol measurement data has been traditionally done manually, which is very time consuming and not a very objective way to make such an analysis. Vuollekoski and Junninen (abstract in this collection) have developed an automatic method that identifies the occurrence of NPF from measurement data. The developed algorithm seems promising, but requires some improvements to warrant its routine use in data analysis.

Kontkanen et al. (2016b) investigated the performance of different methods used for determining the particle growth rate by making cluster population simulations. They found that different methods may give different values for the particle growth rate depending on the ambient conditions, properties of condensing vapors, and the size resolution used in the analysis. The differences were generally largest at the smallest, sub-2 nm sizes and under the conditions where evaporation and other losses were significant.

Hong et al. (abstract in this collection) investigated how aerosol volatility measurements can be applied for distinguishing between extremely low volatile, low volatile and semi-volatile organic compounds, and whether this volatility-based classification is comparable with that based on aerosol mass spectrometric signatures.

**Hygroscopicity and cloud condensation nuclei**

Hong et al. (2015) investigated the connection between aerosol hygroscopicity, chemical composition and concentrations of low-volatile vapors at SMEAR II. They found that the hygroscopicity of accumulation mode particle increased with increasing sulfate to organic concentration ratio in the aerosol phase, as well as with an increasing oxidation level of the organic aerosol. The bulk chemical composition of the submicron aerosol was found to predict fairly well the hygroscopicity of both Aitken and accumulation mode particles, but not that of nucleation mode particles. The hygroscopicity of nucleation mode particles seemed to increase with an increasing concentration of gaseous sulfuric acid.

Paramonov et al. (2015) made a synthesis on Cloud Condensation Nuclei Counter (CCNC) measurements at 14 locations around the world. The work compiled data on measured CCN number concentrations at five levels of water vapor superstation and analysed how the resulting CCN spectra are related to the total particle number concentration, particle number size distribution and particle hygroscopicity. The analysis confirmed, in agreement with some previous studies, that while detailed information on aerosol hygroscopicity can significantly improve CCN predictions, the total particle number concentration and size distribution are more important variables in this respect. The sites having long-term CCN measurements showed clear seasonal and diurnal variability in aerosol hygroscopicity and CCN concentrations, highlighting the spatial and temporal variability of resulting aerosol-cloud interaction in the lower troposphere.
**Vertical mixing, clouds and aerosol-cloud interactions**

Manninen et al. (abstract in this collection) used Doppler radar measurement to investigate how data from this instrument can be used in order to characterize vertical mixing and its time evolution in the continental boundary layer. This method development work is currently under progress.

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.

Tabakova et al. (abstract in this collection) have investigated interactions between biogenic secondary organic aerosols and warm low-level clouds in a boreal environment based on data collected during the Biogenic Aerosols – Effects on Clouds and Climate (BAECC) campaign. The analysed data include adiabatic liquid water content gradient, dilution coefficient and cloud depth, with an aim to develop a methodology for robust data selection to separate the effect of meteorological factors and boundary layer state from the aerosol loading effect.

Aerosol effects on shallow clouds have been studied widely in recent decades, but deep convective clouds have received much less attention. Bister and Kulmala (2011) proposed that aerosol effect on microphysics of deep convective clouds may increase upper tropospheric humidity in convectively active areas. Riuttanen et al. (2016) investigated this topic using satellite data and demonstrated a potentially large positive radiative forcing due to this effect in the global troposphere.

**Integration and large-scale applications**

Where the natural and atmospheric aerosol formation has been intensively investigated during the last decades around the world, less attention has been put to improve quantification of direct anthropogenic particle number emissions. Paasonen et al. (2016) have implemented in GAINS emission scenario model (Greenhous gas – Air pollution Interactions and Synergies; Amann et al., 2011) size segregated emission factors for particle numbers. The first global gridded PN emissions in 9 size bins made publicly available at [http://www.iiasa.ac.at/web/home/research/researchPrograms/air/PN.html](http://www.iiasa.ac.at/web/home/research/researchPrograms/air/PN.html). The GAINS particle number emissions have also been introduced to global climate model in order to compare the resulting concentrations with observations (Xausa et al., abstract in this collection).

Pan-Eurasian Experiment (PEEX) Program ([https://www.atm.helsinki.fi/peex/](https://www.atm.helsinki.fi/peex/)) is an international, multidisciplinary, 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. During the past year, PEEX released conceptual descriptions of the program structure (Kulmala et al. 2015), research agenda (Lappalainen et al. 2016) and in situ observation network (Hari et al. 2016). In implementing the PEEX research approach we have opened the PEEX Special issue in the Journal of Atmospheric Chemistry and Physics ([http://www.atmos-chem-phys-discuss.net/special_issue265.html](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.

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INTRODUCTION

The Atmospheric Modelling group has focus on simulating atmospheric composition, particularly atmospheric aerosol particles, their effects on climate, health, and air quality. The group have done extensive work on developing aerosol microphysics descriptions for large scale models and have developed an aerosol microphysics module SALSA which has been implemented in a cloud resolving model UCLA-LES, air quality model MATCH, and an aerosol-chemistry climate model ECHAM-HAMMOZ. Thanks to its scalability, it has been applied also in process scale studies, for theoretical analysis and chamber studies. The group has also been involved in the Cern CLOUD chamber studies, which have brought several scientific breakthroughs regarding the effect of aerosol formation on climate (e.g. Rondo et al., 2016; Lehtipalo et al., 2016; Duplissy et al., 2016).

CLOUD SCALE MODELLING

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 a large eddy simulations model UCLA-LES, which can be used in simulation processes occurring in sub-grid scale of a global scale model (Maalick et al., 2016; Tonttila et al., 2016). We have implemented an interactive aerosol-cloud microphysics scheme which is an extension to the SALSA model. It includes all aerosol microphysical processes together with cloud activation of the aerosol, ice nucleation, melting, and deactivation of cloud droplets. Figure 1. shows a 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.

One application of the model was to analyze how changes in aerosol properties affect the fog life cycle, with special emphasis on how droplet concentrations change with cloud condensation nuclei (CCN) concentrations and on the effect that absorbing black carbon (BC) particles have on fog dissipation (Maalick et al., 2016). The aerosol effect was found to have a significant effect with respect to when the fog dissipated. In our test cases aerosol prolonged the dissipation by over one hour, which can significantly affect for example air traffic as delays at airports.
GLOBAL SCALE MODELLING

The group has been a major contributor to the development of aerosol-chemistry-climate model ECHAM-HAMMOZ being in the consortium which jointly develops and distributes the model. Recent developments include new parameterizations of aerosol processes. For example, it was the first aerosol-chemistry-climate model to be applied to study amine enhanced nucleation based on the Cern CLOUD studies in the global scale (Bergman et al., 2015). Our study showed that amine-enhanced nucleation is very much confined near the source regions of amines.

Having an own global model configuration with ECHAM-HAMMOZ-SALSA has allowed the group to be involved in the AeroCom-project, which is an open international initiative aiming for improved knowledge of the impacts of atmospheric composition on climate. The group has been involved in several global aerosol model intercomparison experiments. Recently finished experiments in which ECHAM-HAMMOZ-SALSA model has been included are:

- Evaluation of observed and modelled aerosol lifetimes using radioactive tracers of opportunity and an ensemble of 19 global models (Kristiansen et al., 2016).
- What controls the vertical distribution of aerosol? Relationships between process sensitivity in HadGEM3-UKCA and inter-model variation from AeroCom Phase II (Kipling et al., 2016).

With this model framework, we have studied the pros and cons of aerosol emission controls. We used the model to simulate what would happen if every nuclear power plant on Earth were swapped for a coal plant. We assessed the impacts of carbon dioxide emissions and particulate matter on climate, as well as the human health effects of particulate matter smaller than 2.5 micrometers in diameter. Our results showed that the replacement of nuclear power with coal power would have globally caused an average of 150,000 premature deaths per year during the period 2005-2009 with two thirds of them in Europe (Mielonen et al., 2015).

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 fil-
tering anthropogenic contribution to aerosol optical depth using tropospheric NO$_2$ 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 forma-
tion 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., 2016).

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Jülich, University of Oxford, and the Finnish Meteorological Institute and managed by the Center
for Climate Systems Modeling (C2SM) at ETH Zurich.

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PAN-EURASIAN EXPERIMENT (PEEX) PROGRAM - FUTURE PROSPECTS

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Keywords multidisciplinary approach, multiscale research, grand challenges, arctic-boreal, observation networks, land-atmosphere interactions

Pan-European Experiment (PEEX) Program (https://www.atm.helsinki.fi/peex/) is an international, multi-disciplinary, multiscale bottom-up initiative established in 2012 (Lappalainen et al. 2014). The main focus of the initiative is to solve interlinked global environmental challenges influencing societies in the Northern Eurasian region and in China (Kulmala et al. 2016). PEEX also aims to deliver novel ground-based land-atmosphere data for constructing reliable early warning systems, for predicting extreme weather events and for estimating environmental contamination of industrial accidents across the Northern Eurasian region. The program involves research communities from 20 different countries from Europe, Russia and China. Altogether 80 institutes have contributed to the PEEX Science Plan. PEEX is coordinated by the University of Helsinki and the Finnish Meteorological Institute together with the Moscow State University (MSU) and AEROCOSMOS from Russia and Institute of Remote Sensing and Digital Earth (RADI) and University of Nanjing from China.

In years 2012-2016 PEEX has released conceptual descriptions of the program structure (Kulmala et al. 2015), the research agenda (Lappalainen et al. 2016) and the in situ observation network (Hari et al. 2016). In
implementing the PEEX research approach we have opened 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.

Starting from 2012 PEEX has made preparatory work with the Russian station networks and collected the preliminary information on the in situ station measurements over 170 stations stations (Alekseychik et al. 2016). In 2017 PEEX will focus on more detailed metadata inventory of the Russian in situ stations as a part of the EU Horizon 2020 Arctic infrastructure INTAROS project. The metadata overview will the first step connecting the Russian RI to international research infrastructure frameworks. In addition to the upgrading plans of the exiting station infra, PEEX is actively promoting the establishment of new in situ stations in Russia and in China, which would be based on the so called SMEAR (Stations measuring the Earth surface Atmosphere Relations) measurement concept (Kaukolehto et al. 2016). As a part of the PEEX station network approach we have published the “PEEX view tool” (http://www.atm.helsinki.fi/aapon_demo_php/test15_demo.html). PEEX View Tool enables the comparison between the in situ data and the modelled data. In the future, the PEEX-View is envisioned to be part of the PEEX Modelling Platform and combining multidisciplinary datasets of varying temporal and spatial scales. The PEEX modelling platform concept, the descriptions of the model software together with a specific technological platform and data formats will be released in 2017.

The upcoming Finland’s chairmanship of the Arctic Council starting from 2017 sets the PEEX focus on circumpolar collaboration. In 2017 PEEX will expand it’s collaboration across polar areas and, as a first activity, will organize the circumpolar Arctic Flux workshop together with USA and Canadian research groups. The circumpolar Arctic Flux WS will take place in Hyytiälä, Finland on 6-9.Feb.2017. The workshop will be arranged in parallel with the CRUCIAL “Critical steps in understanding land surface – atmosphere interactions: from improved knowledge to socioeconomic solutions” meeting, which would also fostering communication on future Arctic observation systems between USA, Canada, Nordic and Russian research communities. CRUCIAL is a new Nordic-Russia collaboration project coordinated by University of Helsinki Atmospheric Sciences, funded by Nordforsk, starting in autumn 2016.

PEEX organized the second Science Conference in Beijing in May 2016 (Lappalainen et al. 2016b). The conference gathered several new Chinese research contributors representing several branches of the environmental sciences. In 2017 PEEX will continue deepening the collaboration with these Chinese research groups and release a specific PEEX-China research agenda. PEEX recognizes here the unique opportunity to explore cooperation in the sustainable development of environments along the Silk Road Economic Belt and Road. Thus the focus of the PEEX-China research agenda will be on the detailed identification of the environmental challenge of the Belt and Road region.

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EARTH SYSTEM MODELING

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Keywords: EARTH SYSTEM MODEL, CLIMATE, GLOBAL MODELS.

The Earth System Modeling group is responsible for bringing several ATM activities to the global scale by using Earth System Models (ESMs). The group activities cover wide scientific scope from aerosols to greenhouse gases, from natural to anthropogenic emissions, and from small scale processes to global circulation and climate feedbacks. The group develops Earth System Models, including new process descriptions and modules. Tools are developed for thorough evaluation of model components against Earth System observations. The model systems are used for assessing research questions in paleoclimate, historic and future timescales.

The main tools of ESM group are three models, Max-Planck Institute Earth System Model (MPI-ESM), Norwegian Earth System Model (NorESM) and European Earth System Model (EC-Earth). As shown in Table 1, the models are historically rather distinct, and their submodels provide an extensive multimodel platform for the group.

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|}
\hline
        & Atmosphere & Land-vegetation & Ocean \\
\hline
MPI-ESM & ECHAM & JSBACH & MPI-OM \\
NorESM & CAM & CLM & MICOM \\
EC-Earth & IFS & LPJ-GUESS & NEMO \\
\hline
\end{tabular}
\caption{Earth System Models used in the group and their main components.}
\end{table}

Selected research results and future prospects

On the process-level, the ESM group continues developing and implementing new process descriptions to models. The group is testing several potential mechanisms for neutral and ion-induced, as well as organic and in-organic nucleation in global scale. New methods are implemented for secondary organic aerosol (SOA) formation. Recently, the group developed a SOA module to account for extremely low volatility organic compounds (ELVOCs) and their role on nucleation and subsequent growth (Jokinen et al., 2015).

Biosphere-atmosphere interaction has a strong emphasis in the groups research. The group has provided an ESM assessment of BVOC-aerosol-climate interactions over the Tibetan plateau (Fang et al., 2015). It was hypothesized that aerosol-climate interactions might play a considerable role in observed trends of regional precipitation. The group is implementing mechanisms of wetland methane emissions in MPI-ESM land component JSBACH.

Anthropogenic emissions of aerosol and their precursors are likely experiencing substantial changes in next decades. To better account for effects of anthropogenic emissions on climate, the group further develops the emission modules in terms of their chemical and physical characteristics. Xausa
et al. (2016) implement a new framework for size-segregated particulate emissions based on state-of-the-art inventories from GAINS model (Paasonen et al., 2016). The results from their experiments shows substantial improvement of the simulated size distribution in regions close to anthropogenic emissions, especially in terms of Aitken and accumulation mode aerosol number concentrations. The group has addressed the role of changing Arctic human activities on climate: Shcherbinin et al. (2016) includes ECHAM-HAM simulations of 2010-2030 period with increasing emissions in Yamal peninsula. These simulations show that potential increase in black carbon emissions from flaring can have a strong climate impact through Arctic system components.

The group assessed high-latitude Earth System feedbacks in CRAICC project (manuscript in preparation). NorESM was used to simulate e.g. effect of land-use change on atmospheric chemistry and aerosol formation and effect of warming climate on BVOC-aerosol-climate feedback. The group has participated in assessing the effect of aerosol-cloud interactions on upper-tropospheric humidity (Riuttanen et al., 2016) with global climate model experiments.

Makkonen and Krüger (2016) provide a model assessment of 2000-2010 cloud condensation nuclei concentrations (CCN) variability. The apply global aerosol-climate model ECHAM-HAM to quantify trends and variability of CCN. The model can reproduce most of analyzed anomalies in observed CCN concentrations, if both emission and meteorological variability is accounted for. Several analyzed regions including Mediterranean, East and West of US, indicate strong negative trends during 2000-2010, especially after 2005.

The evaluation of components and processes in global Earth System Models is a demanding task in terms of amount and type of data, as well as standards and procedures in model validation. In collaboration with the PEEX initiative, the group has developed PEEXView, an online visualization-analysis tool which combines data from ATM/PEEX infrastructure to global models in ESM group.

The research of the group has been included in earlier aerosol-climate effect quantifications of IPCC assessment report (AR5). For the ongoing CMIP6, which will likely support IPCC AR6, the group is committed to experiments in the DECK and AerChemMIP frameworks (Keskinen et al., 2016). The CMIP6/AerChemMIP experiments will be done in collaboration with FMI and KNMI.

**National and international collaboration and links to research infrastructures**

The ESM group is collaborating with several groups from ATM in order to 1) provide global assessments of FCoE processes, 2) utilize state-of-the-art laboratory and field observations and 3) maximize ESM research impact. The collaboration with Computational Aerosol Physics group links the molecular scale models of cluster formation to nucleation modules in ESMs. Through the collaboration with Atmospheric Mass Spectrometry group the ESM group has been able to implement laboratory results on SOA formation to global aerosol modules. The collaboration with Aerosol-Cloud-Climate Interactions group provides a link to newly established parameterizations and expertise of atmospheric aerosol phenomena. The collaboration with FMI Kuopio unit is essential in terms of ECHAM-SALSA application and development. Finally, strong collaboration with the Dynamic Meteorology group has been essential in linking the Earth System process understanding to impacts on atmospheric circulation.

MPI-ESM collaboration connects the group to Max Planck Institute for Meteorology, Center for Climate Systems Modeling at Eidgenössische Technische Hochschule Zürich and University of Oxford. NorESM is developed in collaboration with the Norwegian Meteorological Institute, University of Oslo and Stockholm University. The community of EC-Earth model spans over ten countries in Europe.

The ESM group activities are strongly linked to national, Nordic, European and global networks, projects and infrastructures. The ESM group is heavily involved in EU FP7 project BACCHUS,
which has provided resources for development and application of MPI-ESM and NorESM. The Nordic collaboration in Earth System Modeling has been supported by e.g. Nordforsk CRAICC, eSTICCC and NordicESM projects. Through eSTICCC mobility funding, the ESM group has received two collaboration visits during 2015. Juan Camilo Acosta-Navarro from Stockholm University visited the group to work on land-use-climate interactions with the NorESM model. The visit by Roland Schrödner from Lund University strengthened collaboration on global simulation and assessment of primary biological aerosol particles. The PEEX initiative provides a platform international collaboration for ESM group research.

The Earth System Models are run at CSC supercomputers, and CSC resources and expertise are used to implement the whole model workflow under CSC computing infrastructure. The on-site support from CSC has proven fundamental for designing and implementing ESM systems on HPC platforms. CSC supports the implementation of a national Earth System Grid Federation (ESGF) node, which will provide researchers a pathway for global open distribution of climate model data.

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

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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. The Greenhouse gases, Micrometeorology 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. The work is done in close co-operation with other FCoE research teams from University of Helsinki (Urban meteorology, Ecosystem processes, Soil Dynamics), from Finnish Meteorological Institute (Greenhouse gases), as well as with other national and international collaborators. 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 is actively involved in several activities related to GHG measurement techniques, protocols and data harmonization within ICOS and other international projects. The work includes advances in 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. 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 another 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. We recommend two flux errors with clear physical meaning: the flux error of the co-variance, defining the error of the measured flux as one standard deviation of the random
uncertainty of turbulent flux observed over an averaging period of typically 30 min to 1 hour duration; and the error of the flux due to the instrumental noise. We suggest that the numerical approximation by Finkelstein and Sims (2001) is a robust and accurate method for calculation of the first error estimate. For the error due to instrumental noise the method by Lenschow et al. (2000) is useful in evaluation of the respective uncertainty.

Finally, an international field instrument intercomparison was implemented at Lake Vanajavesi (Finland) in January-August 2016 (Provenzale et al., 2016). The aim was to evaluate the performance of a new eddy covariance (EC) instrument called the 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 CO\textsubscript{2} 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 (CS\textsubscript{2}) 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 22 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 (CO\textsubscript{2}), water vapour (H\textsubscript{2}O) 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 CO\textsubscript{2} fluxes (Erkkilä et al., 2016a). 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 were 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. The full budget of OCS will be considered by scaling up the soil and branch measurements to the ecosystem level.

Greenhouse gas exchange over lake

Advancing our understanding on physical processes controlling turbulent exchange of energy, carbon dioxide, methane and other trace gases over lacustrine systems is crucial in order to improve climate and weather forecast models. Recent studies have reported that inland waters on the terrestrial landscape generate significant emissions of carbon dioxide and methane (Huotari et al., 2011; Bastviken et al., 2011; Reignier et al., 2013). 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 CO\textsubscript{2} and CH\textsubscript{4} and other auxiliary measurements over the lake and in the water (Mammarella et al., 2015). We aim to assess the current global CO\textsubscript{2} 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). 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) the effect of synoptic

weather events associated with cold front passage, which create a positive pulse in sensible and latent heat

fluxes, as well as in CO2 emission (Mammarella et al., 2016b).

Fluxes of CH\textsubscript{4} and CO\textsubscript{2} were 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., 2016b). 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 remote and large areas, like West Siberia, current estimates of greenhouse gas emission rates are largely

uncertain, because discontinuous and short-term observations (static chamber technique) have been often

used to derive regional and long term emission rates (e.g. Glagolev et al., 2011; Sabrekov et al., 2013).

Current climate models do not explicitly include northern peatland and aquatic ecosystems, because

relationships between driving environmental parameters, small scale processes and fluxes are poorly

known. In order to address these relationships, long-term field observations at different spatial and

temporal scales, intensive measurement campaigns, laboratory experiments, and theoretical framework for

the process based models are needed.

In this respect, 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 Siberia (or at least within a radius of several

thousand kilometres). The obtained fluxes, 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 the wetland site (Alekseychik et al., 2016).

MODELLING STUDIES

Lake modeling

The ability of a lake model to properly simulate surface heat balance, surface and bottom temperatures and

the deepening of thermocline is crucial, because these factors drive the production, consumption and

transport of greenhouse gases in the water column. Besides the atmospheric forcing, the thermal

stratification of the lake depends also on the lake water characteristics, e.g. on the water clarity (Heiskanen

et al., 2015). The model LAKE has been recently advanced to account also for the key processes related to

biogeochemistry (Stepanenko et al., 2016). The model is able to reproduce temperature, methane, carbon

dioxide, oxygen in the water column. The model was validated using data collected at Lake-SMEAR.

Wetland methane model

We have built up a model that takes as input the rate of anoxic peat respiration and computes the

subsequent CH\textsubscript{4} emissions of a peatland by simulating the transport of CH\textsubscript{4}, O\textsubscript{2} and CO\textsubscript{2} and the oxidation

rate that depends on the prevailing O\textsubscript{2} concentration. The aim was to obtain a robust and flexible module

that can be used as a submodel within different soil carbon models. The model HIMMELI (HelsInki
Model of MEthane buiLd-up and emIssion) is driven with peat temperature, leaf area index (LAI) of aerenchymatous gas-transporting vegetation and water table depth (WTD), and it needs as input the carbon (C) input rate, i.e., the rate of anoxic respiration per 1 m² of the peatland. The anoxic respiration rate needs to be simulated with another model. 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 as well as the fraction of oxidized CH₄. For results, see the abstract by M. Raivonen.

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MICROBIAL AND BIOGEOCHEMICAL PROCESSES UNDERLYING SOIL GREENHOUSE GAS FLUXES


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OVERVIEW

Soil microbial processes play and important role in the production and consumption of greenhouse gases. Soils are identified as sources of several trace gases, such as carbon dioxide (CO2), methane (CH4), nitrous oxide (N2O), biogenic volatile organic compounds (BVOCs) and volatile organic nitrogen (VONs), which play an important role in the climate change, in air quality and in tropospheric chemistry.

Continuous long-term measurements at SMEAR I (Eastern Lapland) and SMEAR II (Hyytiälä) stations provide a platform for our process level studies water, material and gas fluxes and the processes underlying them. We have also carried out measurement campaigns in Northern Canada in 2015 and Siberia 2016 for studying GHG fluxes from permafrost soils exposed to forest fire in the Academy of Finland funded project ARCTICFIRE (Pumpanen & Berninger et al.). Another major campaigns carried out in the group in 2015-2016 are the campaigns for studying the CH4 emissions from trees (METAFOR project by Pihlatie et al.) and the trenching plot experiment for studying the contribution of roots and ectomycorrhizal fungi on the decomposition of soil organic matter and nitrogen cycle (NITROFUNGI project by Heinonsalo et al.).

HIGHLIGHTS

The group has produced 31 scientific articles in international peer reviewed journals in 2015-2016 and ca manuscripts 11 are under review. A new Academy of Finland research fellow project was awarded for Mari Pihlatie in 2015 and for Kajar Köster in 2016. Jukka Pumpanen was appointed as a full professor in microbial biogeochemistry at the University of Eastern Finland in October 2015.

NEW RESULTS

Priming effects and decomposition of soil organic matter
J. Heinonsalo, H. Sun, M. Santalahti, K. Bäcklund, P. Hari, K. Karhu, C. Biasi, J. Pumpanen
We showed that the presence of plant induced a significant release of nitrogen (N) from SOM, in a similar way as did oxidative and proteolytic enzymes (Kieloaho et al. 2016) and that certain ectomycorrhizal fungi can utilize organic N that is widely available in SOM, and also deliver the N released from these organic compounds to its host tree. Recently, we have also shown in a three-year long field experiment, using a combination of a trenching experiment and natural C isotopes (13C and 14C) that the priming effect, the plant-induced additional SOM decomposition, may range from +58% to even as high as +185%, compared to heterotrophic soil respiration in the absence of plant roots (Heinonsalo et al. 2016). The abundance of the studied fungi correlated well with the primary production of the forest site, indicating that the belowground activities of N uptake from SOM may be tightly connected to the photosynthetic activities of the host trees, linking SOM decomposition and photosynthesis together (Heinonsalo et al. 2015). Further, we investigated the link between mycorrhizal symbiosis and plant photosynthesis, and found out that the main factors affecting the host plant’s C assimilation capacity were the availability of N and water, not the belowground C demand that has earlier been suggested to be the main mechanism how symbiotic fungi affect plant C assimilation (Heinonsalo et al. 2015).

As a conclusion from our studies we propose that SOM decomposition is tightly connected to the presence of plants and the SOM decomposition in boreal, N limited ecosystems is triggered by the N demand of trees: to increase their N availability, trees need to allocate significant amounts of C belowground, and using these easily available and utilizable carbohydrates, soil microbes can increase the production of their extracellular enzymes that are needed to degrade SOM and release N from organic complexes. We also observed that the relative magnitude of the priming effect increased with soil depth (Karhu et al. 2016) which indicates that the decomposition of SOM in deeper soil layers could be significantly increased due to priming, if labile carbon inputs into these layers increase.

Effects of disturbances on soil GHG fluxes, carbon cycle and soil microbial processes
K. Köster, F. Berninger, J. Heinonsalo, H. Sun, F. Asiegbu, E. Köster, M. Palviainen, H. Aaltoenen, X. Zhou and J. Pumpanen

We are studying the effects of forest fires on GHG fluxes and soil organic matter decomposition on permafrost and non-permafrost soils in Finland, Canada and Russia. Our first results indicate that forest fires decreases the turnover rate of carbon because significant amounts of organic matter in the surface soil is combusted and the microbial population is decreased. This is because of the heating of the surface soil and death of trees which sustain ectomycorrhizal fungi. We observed that the enzyme activities in the soil surface are decreased immediately after fire and the microbial activity recovered slowly along with the accumulation of organic matter on the soil surface (Köster et al. 2016). Forest fires also affected the GHG fluxes; net CO2 emissions and CH4 uptake were increased, but no significant effect on N2O fluxes were observed as a result of fire. The uptake of CH4 partly compensated the increase in radiative forcing resulting from the CO2 emissions at the recently burned sites, but the compensating effect was very small (Köster et al. 2015). We also observed that the microbial community structure was affected by the fire. Based on DNA-sequencing, the fungal community was more diverse soon after fire disturbance and declined over time. Based on functional gene array technique the genes involved in organic matter degradation in the mature forest, in which ECM fungi were the most abundant, were as common in the youngest site, in which saprotrophic fungi had a relatively higher abundance (Sun et al. 2015). We also carried out the same analyses for bacterial community and observed that the bacterial diversity did not differ between the recently and older burned areas, suggesting a concomitant recovery in the bacterial diversity after fires. Soil temperature, pH and water contents were the most important factors in shaping the bacterial community structures and function (Sun et al. 2016). The studies provide functional insight on the impact of fire disturbance on soil bacterial community.

Reindeer is the most important mammalian herbivore in the northern latitudes which strongly effects on the arctic ecosystems. We are studying the effect of reindeer on soil GHG (CO2, CH4 and N2O) fluxes and its underlying factors in subarctic forests in Finnish Lapland. Reindeer grazing decreased the biomass and cover of lichens and decreased the tree regeneration, but did not affect the soil CO2 efflux, soil C stock,
and the soil microbial C biomass. Thus, from carbon balance point of view, reindeer grazing can be considered carbon neutral (Köster et al. 2016).

Short term effects of biochar on carbon cycling in boreal Scots pine forests

Data on the effects of biochar on soil carbon turnover is important in boreal forests where large quantities of forest harvest residues would be available as feedstock for biochar production. In order to better understand the effects of biochar on forest soil we established a factorial experiment where two different spruce biochars were applied at the rate of 1.0 kg m\(^{-2}\) and 0.5 kg m\(^{-2}\) in a young xeric Scots pine forest of southern Finland. Biochar application increased the rate of soil respiration by 11\%, however, microbial biomass did not differ between the treatments. We concluded that increase in soil respiration was attributed to warmer soils after biochar application to the soil surface while changes in soil chemistry or soil physical properties did not have any detectable effect on respiration.

Soil concentrations and soil-atmosphere exchange of alkylamines in a boreal Scots pine forest
A.J. Kieloaho, M. Pihlatie, S. Launiainen, M. Kulmala, M.-L. Riekkola, J. Parshintsev, I. Mammarrella, T. Vesala and J. Heinonsalo

Alkylamines are important precursors in secondary aerosol formation in the boreal forest atmosphere. To better understand the behaviour and sources of two alkylamines, dimethylamine (DMA) and diethylamine (DEA), we estimated the magnitudes of soil-atmosphere fluxes of DMA and DEA using a gradient-diffusion approximation based on measured concentrations in soil solution and in the canopy air space. Our results show that boreal forest soil is a possible source of DMA and sink of DEA. We also found that fungal biomass may be an important reservoir of alkylamines.

Spring recovery and variation in methane fluxes from boreal trees in southern Finland
I. Haikarainen, E. Halmeenmäki, K. Machacova, M. Pihlatie

Trees are noted to be capable of transporting microbially produced methane (CH\(_4\)) from anaerobic soil conditions to the atmosphere. We measured the variation in tree CH\(_4\) flux during the spring 2015 from stems and shoots of downy birches (Betula pubescens) and Norway spruces (Picea abies) in Hyytiälä. Methane was emitted from stems and shoots of both tree species, and emissions were generally higher from birches than from spruces. Methane emission rates from birches correlated positively with soil temperature and also increased as the growing season proceeded. Trees living in the boreal region are capable to emit CH\(_4\), but the mechanisms remain unresolved as well as temporal and spatial variation in CH\(_4\) fluxes between the tree species.

Daytime emission and night-time uptake characterize CO fluxes from an agricultural bioenergy crop M. Pihlatie, Ü. Rannik, S. Haapanala, O. Peltola, N. Shurpali, P.J. Martikainen, S. Lind, N. Hyvönen, P. Virkajärvi, M. Zahniser, and I. Mammarrella

We report the first long-term and continuous field measurements of CO fluxes using the micrometeorological eddy covariance (EC) method. We demonstrate that the EC method is suitable in identifying seasonal and diurnal variability as well as driving variables of CO fluxes at ecosystem level. The daytime CO emissions were mainly driven by direct and indirect effects of radiation, while the night-time CO uptake was connected to N\(_2\)O emissions. In order to fully understand the source-sink dynamics and processes of CO exchange, continuous and long-term flux measurements in combination with process-based studies are urgently needed.

Seasonal courses of methane fluxes in boreal trees
K. Machacova, E. Halmeenmäki, M. Pihlatie, and O. Urban
Recent studies have shown that plants can significantly contribute to the CH$_4$ exchange between ecosystems and the atmosphere, but investigations on trees, particularly boreal tree species, are still rare. Seasonal CH$_4$ fluxes from stems of common boreal tree species – Scots pine (Pinus sylvestris), Norway spruce (Picea abies) and downy and silver birch (Betula pubescens, B. pendula) – and the forest floor, were determined. Our results show that mature boreal trees exchange CH$_4$ with the atmosphere throughout the whole year with minimum and maximum fluxes during dormant and vegetation period, respectively, and the fluxes are modulated by soil water content. The tree species studied emitted CH$_4$ mainly during the vegetation season, however, considerable emissions were detected already from February onwards. The stem CH$_4$ emissions of trees may reduce the sink strength of soils in boreal forests.

Comparison of the above canopy and the forest floor methane flux modelled by soil water content
E. Halmeenmäki, I. Haikarainen, O. Peltola, M. Pihlatie

The upland soils have a capacity to emit CH$_4$, when soil moisture is at adequate level, and also vegetation has been found to contribute to the ecosystem-atmosphere CH$_4$ exchange. The sources and the mechanisms of the observed CH$_4$ emissions from the forests are still mostly unknown. By utilising lidar data and in situ measurements of CH$_4$ fluxes and soil moisture, we have modelled the potential CH$_4$ flux of a boreal forest floor. The potential forest floor CH$_4$ flux will be compared to the measured above canopy CH$_4$ flux.

PUBLISHED PEER REVIEWED PAPERS 2015-2016:


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SUBMITTED MANUSCRIPTS:


Sampling and analysis of organic compounds and their reaction products in chamber and boreal forest atmosphere

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Keywords: Alkylamines; monoterpenes; reaction products; amino acids; soil emissions; determination

INTRODUCTION

Terrestrial vegetation introduces to the atmosphere an enormous diversity of biogenic volatile organic compounds (BVOCs), which consist of a large variety of molecules that differ in size, physicochemical properties and metabolic origin (Peñuelas and Staudt, 2010). Some BVOCs, such as monoterpenes, are oxidized in the atmosphere and the oxidation products formed can participate in the formation of secondary aerosol particles (SOA) (e.g. Riipinen et al., 2012). Other organic volatiles, including aldehydes, take part in atmospheric photolytic reactions and contribute to new particle formation (Hellén et al., 2004).

Amines are emitted to the atmosphere from industry, combustion, biomass burning, animal husbandry and oceans. In addition, soil and vegetation act as important sources of amines, especially during periods with high biological activity. These compounds are ubiquitous in the atmosphere and observed in several locations in the world, for example Ge et al. (2011) summarized 154 identified amines in the atmosphere emitted from anthropogenic and biogenic sources. The most abundant amines in the atmosphere are low-molecular weight aliphatic amines such as methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA). More recently, laboratory and field studies have shown the formation of nitrogen-containing low volatile compounds in pinonaldehyde-dimethylamine reaction (Duporté et al., 2016), suggesting the potential role of amine on oxidation products of α-pinene in the atmosphere.

Primary biological aerosol particles (PBAPs) include e.g. pollen, fungal spores, bacteria, viruses and cell fragments of plants and animals are emitted to the atmosphere from vegetation and other living organisms (Després et al., 2007). Their importance to atmospheric chemistry and physics has increased interest towards their reliable determination. PBAPs are considered to be a major source of proteinaceous materials in the atmosphere (Matos et al., 2016). It is suggested that proteins have undergone enzymatic hydrolysis or thermal or photochemical decomposition into peptides or free amino acids (FAAs). Amino acids can serve as markers for various kinds of PBAPs.

METHODS

BVOC measurements from soil chambers were performed in summer 2015 at the Station for Measuring Ecosystem-Atmosphere Relations, SMEAR II in Hyytiälä, Finland. The first part (testing and optimization of the method) of the campaign occurred from 23rd to 28th of June where conventional GC-MS was used. The second part (sampling and analysis of BVOCs from soil chambers and ambient air) of the campaign occurred from 5th to 27th of August where SPME and portable GC-MS was utilized. Sampling was performed by SPME syringes (DVB/PDMS, 65μm film thickness). Chambers were closed and SPME fibers placed inside the soil chambers for 40 min passive collection. Ambient air samples were collected for 60 min using two dynamic SPME sampling system (flow rate of 11 L/min) simultaneously at 30 cm height from the ground vegetation (Barreira et al., 2015, 2016). A comparison between portable and conventional GC-MS analysis was performed by simultaneous 40 min collection of two SPME samples from the chamber.
Reactivity experiments to investigate the effect of amines on the α-pinene ozonolysis reaction were performed in a flow tube reactor. The gas phase was on-line monitored by high resolution chemical ionization mass spectrometry (HR-LTOF-CIMS). Aerosols were sampled on 47 mm PTFE filters at a flow rate of 1 L/min. Structures of the reaction products were determined by ultra-high-performance liquid chromatography coupled to electrospray Orbitrap mass spectrometry (UHPLC-ESI-HRMS). Particle size distribution was measured with a scanning mobility particle sizer (SMPS). To support the results of laboratory experiments, ambient aerosol samples (PM1) were collected from SMEAR II boreal forest site at Hyytiälä, Finland, during May-June 2016 and analysed by the same analytical methodologies.

The aerosol samples for the determination of free amino acids (FAA) were collected between February and October 2014 at the SMEAR II station in Hyytiälä, Finland. A Dekati PM10-impactor was used for the sampling of four particle size fractions (<1.0, 1-2.5, 2.5-10 and >10 µm). The sampling flow rate was on average 29 L/min and the collection time was from two to four days (sampling volume 76-144 m³). Polycarbonate membrane filters (25 mm) smeared with diluted vacuum grease were used for the three largest particle size fractions. The smallest size fraction (<1.0 µm) was collected on a 47 mm teflon filter with 2 µm pore size. After sampling, the filters were dried, placed inside a closed petri dish and stored in -20 °C.

Ultrasound assisted extraction with 0.1% formic acid was used for the FAA in the filters. Filters were spiked with known amount of labelled internal standard mixture solution. The sample was sonicated at room temperature for 15 minutes with 2 mL of 0.1% formic acid. Sonication was repeated twice with 2 mL and 1 mL of 0.1 % formic acid for 10 minutes each time. Finally, 1 mL of toluene was added into the extract solution to remove grease. The solution was vortexed and centrifuged. Aqueous layer was separated and filtered through a 0.45 µm filter into a 5 mL volumetric flask. The samples were stored at 4 °C and analyzed within 72 hours.

The analyses of FAA were performed with HPLC coupled to triple quadrupole mass spectrometer. Electrospray ionization in positive mode was used. The column used was a SeQuant ZIC-cHILIC (100 x 2.1 mm, particle size 3 µm, 100 Å). The column temperature was maintained at 30 °C and the injection volume was 3 µL. Eluent A was 0.01% acetic acid in acetonitrile and eluent B was 0.01% acetic acid in ultrapure water. The optimized gradient program was as follows: 0-10 min, 20% eluent B; 10-20 min, 60% eluent B; 20-40 min, 60% eluent B; 40-45 min, 20% eluent B and equilibration for 25 min. The flow rate was 150 µL/min. The MS was operated in a dynamic multiple reaction monitoring (MRM) mode. Mass spectrometer source parameters were optimized, and fragmenter voltage, collision energy and cell accelerator voltage were optimized for each amino acid separately.

For analyzing the importance of the sampling time and the aerosol filter size, multivariate analysis of variance (MANOVA) was performed for the gene copy numbers of bacteria, Pseudomonas and fungi as well the presence/absence transformed FAAs data. The MANOVA was performed with the adonis-function of the vegan package (Oksanen et al., 2016), and the FAAs and gene copy number data were set as response variables while sampling month and aerosol filter size were set as explanatory variables. In addition, the FAAs data was compared to the gene copy numbers data by means of regression analysis and correlation between each variable was studied. The three largest particle size fractions were included in these data analyses, because the gene copy number data was only analyzed from these size fractions.

CONCLUSIONS

Measurements of BVOCs from soil chambers were performed in summer 2015 at the Station for Measuring Ecosystem-Atmosphere Relations, SMEAR II in Hyytiälä, Finland. Air samples were collected simultaneously from soil chambers and ambient air by static and dynamic SPME, respectively, to compare the type and relative amounts of VOCs found in soil samples with those found in ambient air. Sample preparation was avoided, reducing analysis time, sample contamination and potential losses during analytical process. The most abundant BVOCs measured in chambers and ambient air were α-pinene and
Δ3-carene (Fig. 1). Aldehydes with a recognized role on atmosphere physics and chemistry were also measured (Fig. 2). Agreement between amounts of monoterpenes measured from soil chambers by portable GC-MS and monoterpane fluxes measured by PTR-MS was observed.

Figure 1. Amounts of monoterpenes expressed as peak area, measured by portable GC-MS. Samples were statically collected from soil chambers and dynamically collected from ambient air. Monoterpene fluxes [ng/(m²s⁻¹)] measured from the soil chambers by PTR-MS were included for comparison.

Figure 2. Amounts of aldehydes expressed as peak area, measured by portable GC-MS. Samples were statically collected from soil chambers and dynamically collected from ambient air.
Reactivity between oxidation reaction products of α-pinene, such as pinic acid and pinonic acid, and dimethylamine was observed. Figure 3 presents the temporal profiles of selected ions by HR-LTOF-CIMS. Surprisingly, a significant increase in the concentration of highly oxygenated compounds (see C_{9}H_{14}O_{3}I as an example in Figure 3) after injection of dimethylamine was also noticed in this work. Finally, nitrogen-containing reaction products were identified by HR-LTOF-CIMS (see C_{6}H_{9}NO_{3}I as an example in Figure 3). Interestingly, a subsequent enhancement of the nucleation after α-pinene ozonolysis was seen in the presence of dimethylamine.

Figure 3. Temporal profiles of selected ions by HR-CIMS.

In total, more than 40 nitrogen-containing compounds were identified from the filter sampling in the presence of DMA by Orbitrap LC-MS. Furthermore, five reaction products (C_{11}H_{17}O_{2}N, C_{12}H_{21}NO, C_{11}H_{20}NO_{2}, C_{10}H_{15}NO_{3}, C_{12}H_{21}NO_{2}) in ambient SMEAR II aerosol samples were confirmed. MS^2 fragmentation patterns of m/z 198.1489 ions from α-pinene-O_{3}-dimethylamine experiments and PM1 sample in Hyytiälä are presented in Figure 4.

Figure 4. MS^2 fragmentation pattern of m/z 198.148 ions detected a) in α-pinene-O_{3}-DMA experiments and b) in PM1 sample in Hyytiälä (23.05.2016 day filter)
New products were determined and identified for the first time and the reaction products found in ambient aerosol particles suggest that dimethylamine may play an important role in the formation and growth of SOA of secondary organic aerosols after α-pinene ozonolysis in the atmosphere.

The concentration of free amino acids was the highest during late spring and early summer during the pollen season peak, the range being between 0.3 to 2087.8 pmol/m³, when all size fractions were taken into account. In addition, the concentration of FAAs increased again in autumn, when other PBAPs (e.g. fungal spores) emissions reached their maximum concentration (Figure 5). The annual pattern of FAAs concentration was similar to that of PBAP observed previously in the same sampling site (Manninen et al., 2014). Furthermore, similar annual pattern was observed between FAAs and extracted DNA concentration. The amount of extracted DNA was also highest during early summer and autumn (see Sietiö et al., 2015).

![Figure 5. Total concentration of free amino acids in aerosol samples.](image)

The relative concentration of FAAs had different seasonal variation in different particle size fractions. It was highest in the <1 µm fraction during late winter, whereas during the pollen season, amino acids were mainly in the >10 µm fraction. Seemingly during summer months FAAs are more evenly distributed in all size fractions. In autumn FAAs are mainly present in the <10 µm particles.

In the size distribution some clear tendencies were observed, such as high glycine level in the <1 µm fraction and higher glutamine and glutamic acid levels in the <10 µm fractions (Figure 6). Glycine was the most dominant amino acid in the particles <1 µm, whereas in the other size fractions amino acids were more evenly distributed. Figure 6 was plotted without the pollen season samples to get more representative distribution. With the pollen season samples that were dominated mainly by proline and arginine and present in huge concentrations, the distribution would have been distorted.
The results from the MANOVA analysis indicated that seasonal variation explained the observed variation across the whole amino acid and gene copy number data with statistical significance (p<0.001). In addition, the size of the aerosol filter was statistically significant factor for explaining the observed variation (p<0.05). The preliminary results from regression analysis revealed that the concentration of FAAs correlates with the amount of bacteria found in each size fraction: 1-2.5 μm (R²=0.93, p<0.001), 2.5-10 μm (R²=0.86, p<0.001), >10 μm (R²=0.93, p<0.001) and total particles (R²=0.97, p<0.001). However, the correlation between FAAs and bacteria is mainly due to the high abundance of both variables during the pollen season. If the pollen season samples are excluded, the correlation would be negligible although in the total particles there was still borderline statistical significance (R²=0.29, p<0.05). Between FAAs and Pseudomonas or fungi, no statistically significant correlation was observed.

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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.

The recent breakthroughs include:

1) 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 in the preindustrial atmosphere (Kirkby et al., 2016, Nature). The ionization by galactic cosmic radiation readily enhances these new particle formation rates one to two orders of magnitude. This suggests that ion-induced nucleation of pure organic oxidation products may be an important source of new particles in terrestrial environments with low sulphuric acid concentrations.

2) Based on the same experiments as above, we also investigated the role of organic vapors with different oxidation state and volatility in the initial growth of biogenic clusters and new particles (Tröstl et al., 2016, Nature). We find that the organic vapors that drive initial growth have extremely low volatilities (saturation concentration less than $10^{-4.5} \text{ g m}^{-3}$). As the particles increase in size, the Kelvin barrier decreases and subsequent organic vapors of slightly higher volatility (saturation concentrations of $10^{-4.5}$ to $10^{-0.5} \text{ g m}^{-3}$) can condense on the fresh particles. Accounting for these mechanisms of growth, we estimate that concentrations of atmospheric cloud concentration nuclei can change up to 50% in comparison with previously assumed growth rate parameterizations.

3) We measured growth rates at sub-3 nm sizes with different atmospherically relevant concentrations of sulfuric acid, water, ammonia and dimethylamine in the CLOUD chamber, and found that small acid-base clusters, which are not generally accounted for in the measurement of sulfuric acid vapor, can participate in the growth process, leading to enhanced growth rates (Lehtipalo et al., Nature Communications, 2016). This mechanism could be important in amine rich environments and assist the freshly formed clusters to survive the initial steps of growth.

4) In a study by Bianchi et al (Science, 2016) new particle formation (NPF) was studied in the free troposphere on top of Jungfraujoch mountain in Switzerland. It was found that at high altitudes, NPF occurs mainly through condensation of HOM, while observations show also frequent sulfuric acid–ammonia nucleation. Neutral nucleation was found to be the dominant pathway rather than ion-induced nucleation, and this study also found size-dependent growth rates. In general, atmospheric observations regarding the molecular steps of initial cluster formation and early growth are rare, and this is the first study illuminating these processes in free troposphere.

5) In a study performed on the western coast of Ireland, in Mace Head, we for the first time resolved the detailed molecular steps of neutral cluster formation (Sipilä et al., 2016, Nature). We found that cluster formation primarily proceeds via sequential addition of iodic acid (HIO$_3$) and subsequent restructuring to form I$_2$O$_5$, either in the atmosphere or upon drying in the vacuum of the mass spectrometer.
spectrometer. The same mechanism was observed to take place also in spring-time in northern Greenland. Elevated concentrations of HIO$_3$ were observed also at Aboa-station, Antarctica, suggesting HIO$_3$ to potentially be an important source of new particles in polar atmospheres (likely over sea ice).

6) As shown in many of the above papers, HOMs have a significant contribution to secondary aerosol formation, yet their dominating formation pathways remain unclear in the atmosphere. We applied positive matrix factorization (PMF) on HOM data from the SMEAR II station, and successfully retrieved factors representing different formation pathways, including monoterpane oxidation by all the three major oxidants OH, ozone and NO$_3$ (Yan et al., 2016).

ONGOING RESEARCH AND FUTURE GOALS

Current research topics include, but are not limited to, the following broad topics:
- Resolving the precursors and formation mechanisms of HIO$_3$ in polar regions
- Simulating the Hyytiälä day time NPF in CLOUD chamber
- Determining the relative roles of H$_2$SO$_4$ and HIO$_3$ in Antarctic NPF through in-situ measurements
- Determining the temperature dependence of HOM formation from different systems
- Chemometric analysis and long-term variations of SOA in Hyytiälä
- Chamber studies of HOM formation pathways under various conditions
- HOM formation from aromatic compounds

CONCLUSIONS

The research within the Atmospheric Mass Spectrometry group continues to yield high-impact scientific results, as can also be seen from Fig. 1. Already, 2016 has shown to be an exceptional year when it comes to Nature and Science publications.

![Figure 1. Publication merits of mass spectrometry-related research at UHEL until September 2016.](image)

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.
ACKNOWLEDGEMENTS

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IDENTIFYING A PARTICLE FORMATION MECHANISM IN THE ATMOSPHERE

We have provided theoretical basis for analysis of novel field data from Mace Head, Ireland reporting particle formation in an iodine-rich, coastal atmospheric environment. The formation and initial growth process is almost exclusively driven by iodine oxoacids and iodine oxide. On the basis of the high oxygen-to-iodine ratio of 1.4, together with the high concentrations of iodic acid (HIO₃) observed, the cluster formation is suggested to primarily proceed by sequential addition of HIO₃, followed by intracluster restructuring to I₂O₅ and recycling of water either in the atmosphere or on dehydration. This is the first time molecular-level understanding of particle formation has been achieved in atmospheric field conditions (Sipilä et al., 2016).

THEORETICAL UNDERSTANDING OF LABORATORY OBSERVATIONS

We have developed an updated version of the classical nucleation theory for sulphuric acid-water system. The thermodynamic model is normalized to state-of-the-art quantum chemical studies for the smallest neutral clusters, and it is consistently extended to kinetic (barrierless) and ion-induced particle formation. The result show a good agreement with contaminant-free measurements of sulphuric acid-water particle formation rates measured at the CLOUD (Cosmics Leaving OUtdoors Droplets) chamber. We predict that the two-component water-sulfuric acid system can produce particles at a significant rate in the free troposphere both through barrier crossing and through kinetic pathways. At cold stratospheric and upper free tropospheric temperatures neutral formation dominates the formation rates, but at mid-tropospheric temperatures the ion-induced pathway becomes dominant. However, even the ion-induced binary mechanism does not produce significant amount of particles in the warm, above 0°C to boundary layer conditions (Duplissy et al., 2016 and Merikanto et al., 2016).

We have participated in a study on how heterogeneous nucleation of vapour on a seed surface is dependent on the seed properties such as size, chemical composition, and electric charging state. The most important parameter determining the nucleation probability in the sub-3 nm size range was the seed chemical composition, which is connected to the charging state, as these two cannot be varied independently. No systematic sign preference exists for any of the condensing liquids and seeds studied (Kangasluoma et al., 2016).

UNDERSTANDING PARTICLE GROWTH MECHANISMS

We have collaborated in a study reporting and analyzing growth rates of sub-3nm size clusters and particles with different atmospherically relevant concentrations of sulphuric acid, water, ammonia and dimethylamine in the CLOUD (Cosmics Leaving OUtdoors Droplets) chamber. The results show that atmospheric ions and small acid-base clusters, not usually accounted for in the measurement of sulphuric acid vapour concentration, can contribute significantly to the growth process (Lehtipalo et al., 2016).
We continued to assess the validity of approximate methods to determine growth rates of sub-3 nm clusters and the validity of the common approach to use them to estimate formation rates for clusters smaller than the instrumental detection limit. We extended our previous study to a case where clusters do not only grow by condensation of monomers, but cluster–cluster collisions also significantly contribute to the growth. The results show that conventional methods used to determine particle formation rates from growth rates may give estimates far from the real values (Kontkanen et al., 2016).

REFINED STUDIES OF THE SULPHURIC ACID-BASE-WATER SYSTEM

We used quantum chemical methods to study the chemical fate of $SO_3SO_3^-$ formed in a reaction between sulphur dioxide and the sulphate radical at atmospheric relevant conditions. The results show that when $SO_3SO_3^-$ reacts with ozone most of the collisions are non-sticking, the most frequent reactive collisions regenerate sulfate radical ions, and produce sulphur trioxide while ejecting an oxygen molecule (Tsana et al., 2016).

We have performed electronic structure calculations on the hydrates of clusters of three molecules of sulfuric acid and three molecules of ammonia or dimethylamine. Combining the results of these new calculations with previously published material we have studied the sensitivity of the atmospheric particle formation rate for humidity. The particle formation rate can change approximately two orders of magnitude in either direction due to hydration; the net effect, however, is highly dependent on the exact conditions. The ammonia-containing system is more sensitive to relative humidity than the dimethylamine-containing system (Henschel et al., 2016).

We study the performance of a promising domain local pair natural orbital coupled cluster (DLPNO-CCSD(T)) method in calculating binding energies of atmospherical molecular clusters. The DLPNO method significantly reduces the scatter in the binding energy of small complexes of atmospheric relevance, which is a common problem in DFT (density functional theory) calculations. For medium sized clusters consisting of sulfuric acid and bases, the DLPNO method yields a systematic size-dependent underestimation of the binding energy compared to canonical coupled cluster results, indicating that a scaling factor should be applied to improve the predictive power of the method. (Myllys et al., 2016).

ASSESSING THE PARTICLE FORMATION OPETNTIAL OF OXIDIZED ORGANICS

We have investigated the interaction of some highly oxidized organic molecules with sulphuric acid, and find that the heterodimers are more strongly bound than pure sulfuric acid dimers. Their stability correlates well with the oxygen to carbon ratio of the organics, their volatility, and the number of hydrogen bonds formed (Ortega et al., 2016). We also studied the molecular interaction between sulphuric acid and a C$_6$H$_8$O$_7$ ketodiperoxy acid compound (a proxy for highly oxidized products from, for example, monoterpane autoxidation) in the presence of water, ammonia, or dimethylamine. Bases molecules enhance the interaction between ketodiperoxy acid compounds and sulphuric acid. The addition of C$_6$H$_8$O$_7$ compounds to sulphuric acid-ammonia or sulphuric acid-dimethylamine clusters is, however, not able to compete with the uptake of another sulphuric acid molecule, even at a high concentrations of organic compounds, indicating that autoxidation products containing solely or mainly hydroperoxide and carbonyl functional groups are not responsible for particle formation, but could contribute to the growth of atmospheric particles (Elm et al., 2016b).

We have extended the quantum chemical studies previously applied to clustering of sulphuric acid, ammonia, dimethylamine and water to clusters of sulphuric acid and diamines. The diamines studied bind equally or more strongly to sulfuric acid than dimethylamine does. Diamines that contain one or more secondary amino groups stabilize the complex formation with sulfuric acid most efficiently. To fully understand the involvement of diamines in atmospheric particle formation further work on larger clusters is still needed (Elm et al., 2016a).
COUPLING MOLECULAR MODELS TO LARGER SCALE MODELS

Our state-of-the-art molecular level model of particle formation in sulphuric acid-ammonia-water particle formation was coupled via look-up-tables to PMCAMx-UF, a three-dimensional chemical transport mode over Europe for the dates of the EUCAARI-LONGREX campaign in May 2008. The model now reproduces the observed number concentrations of particles larger than 4 nm within 1 order of magnitude throughout the atmospheric column, with no semi-empirical fitting needed to obtain realistic particle formation rates (Baranizadeh et al., 2016).

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UNIVERISTY OF EASTERN FINLAND: AEROSOL-CLOUD INTERACTIONS AND CLOUD MICROPHYSICS

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Keywords: aerosols, clouds, experiments, modelling

INTRODUCTION

Atmospheric aerosols affect both the climate and human health. Hence they are in a key role when the wellbeing of humans and environment is considered. The research of 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 atmospheric water vapour and clouds.

GROUP ACTIVITIES

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

- formation of Secondary Organic Aerosol (SOA) particles both in laboratory and atmospheric conditions (Pajunoja et al., 2016; Yli-Pirilä et al., 2016; Kari et al., 2016)
- interactions between anthropogenic and biogenic emissions (Kari et al., 2016; Tiitta et al., 2016; Kortelainen et al., 2015; Kortelainen et al., 2016)
- physical and chemical characteristic of SOA particles and atmospheric aerosols (Pajunoja et al., 2015; Pajunoja et al., 2016; Hong et al., 2016; Yli-Juuti et al., 2016a; Saukko et al., 2016)
- water up-take and CCN activation of laboratory SOA particles and atmospheric aerosols (Väisänen et al., 2016; Kim et al., 2016, Pajunoja et al., 2015, Hong et al., 2016, Hansen et al., 2016; Dalirian et al., 2016)
- studying how environmental factors change VOC emissions of trees and further the SOA formation (Faiola et al., 2016, Kari et al., 2016b; Joutsensaari et al., 2015).

To investigate these topics more in detail we have performed intensive measurement campaigns using our own facilities: ILMARI facility in studying the interactions between anthropogenic and biogenic emissions, and Puijo SMEAR IV station to study aerosol-cloud interactions. Currently we are running a campaign at Puijo jointly with Helsinki University. The main topic of the current campaign is in studying the cloud processing of aerosols and the partitioning of semivolatile vapors inside the cloud. We have run extensive laboratory measurement campaigns in our Aerosol Physics Lab to study factors controlling the evaporation of SOA particles. This has been complemented by detailed process modelling in order to find out the effect of phase state and intra-particle processes on SOA dynamics. We have also participated in several measurement campaigns in other organizations: at Karlsruhe Institute of Technology (KIT) we have studied the cloud processing of SOA particles utilizing the AIDA cloud expansion chamber and at LISA (Laboratoire Interuniversitaire des Systèmes Atmosphériques) in Paris we studied the chemical transformation and phase state changes of SOA particles during cloud condensation–evaporation cycles.

The modelling activities of the group have been focused on process level modelling related to formation and transformation of atmospheric aerosols, especially the thermodynamics and kinetics of gas-particle partitioning of SOA. The main topics are currently:
Secondary organic aerosols and partitioning of organic vapors (Yli-Juuti et al. 2016a; Tikkanen et al. 2016)
Description of particle phase diffusion limitations (Yli-Juuti et al., 2016a)
Condensational growth of atmospheric aerosols (Hao et al., 2016; Yli-Juuti et al., 2016b; Heitto et al., 2016)
Acid-base systems and their thermodynamic descriptions (Ahlm et al., 2016)
Data analysis of measured aerosol size distribution dynamics to quantify the important participating processes (Lehtinen, 2016).

Our lead 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 will be achieved. This way, we are able to extract from the experimental laboratory data such aerosol properties that would otherwise hide behind the complex nature of the dynamic laboratory experiments and, furthermore, we can evaluate the models for describing aerosol processes in atmospheric conditions.

COLLABORATION

The group’s excellent research facilities and wide collaborative network allows us integrating 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
- Assoc. Prof. Ilona Riipinen, University of Stockholm, Sweden
- Prof. Paul Davidovits, Boston College; USA
- Prof. Douglas Worsnop, Aerodyne Research, USA
- Prof. Gordon McFiggans, University of Manchester; Great Britain
- Prof. Alex Gunther, PNNL, USA
- Prof. Jose Jimenez, University of Colorado, USA
- Prof. Frank Stratmann, Leibniz Institute of Tropospheric Research, Germany
- Prof. Jarmo Holopainen, UEF, Finland
- Assist. Prof. Manabu Shiraiwa, University of California Irvine, USA
- Assist. Prof. Paul Winkler, University of Vienna, Austria.
- Prof. Sergey Nizkorodov and Prof. James Smith, University of California, Irvine, USA.
- Dr. Claudia Mohr, Karlsruhe Institute of Technology, Germany
- Prof. Jean-Francoise Doussin, Paris-Est Créteil University, France
- CLOUD collaboration

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SEASONAL VARIATION IN MONOTERPENE EMISSION CAPACITY OF SCOTS PINE

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Keywords: VOC EMISSIONS, MONOTERPENES, SEASONAL VARIATION.

INTRODUCTION

Seasonality in terpenoid emissions of boreal evergreen tree species is poorly known. The emission potentials, which describe the capacity to maintain emissions under standard conditions, are mostly studied under laboratory conditions or during relatively short campaigns under field conditions. Because comprehensive information on seasonal changes in emission potential is missing, current applications are mostly based on the assumption of constant emission capacities (Staudt et al., 2000, Guenther et al., 2012).

METHODS

The measurements were carried out at SMEAR II –station (Station for Measuring Ecosystem-Atmosphere Relations), located in southern Finland in boreal zone. The monoterpene emission rates of Scots pine shoots were measured under field conditions using an automated gas-exchange measurement system coupled with a proton transfer reaction-quadrupole mass spectrometer (PTR-QMS, Ionicon Analytik GmbH, Innsbruck, Austria). The measurements were conducted during years 2009-2015 and included shoots with 0-, 1- or 2-year old needles from three pine trees. The emission potentials were determined using both conventional evaporation –based temperature approach (e.g. Guenther et al., 1993) and hybrid algorithm approach (Ghirardo et al., 2010, Aalto et al., 2015). The standard conditions in solving the emission potentials were T=30 °C and PPFD=1000 µmol m\textsuperscript{-2} s\textsuperscript{-1}. In both approaches the temperature dependency parameter $\beta=0.09$ K\textsuperscript{-1}.

RESULTS

The results show clear seasonal cycle in the monoterpene emission potential of Scots pine. The maximum in monoterpene emission potential of 1-year old pine shoots takes place during the coldest and darkest winter period, whereas the minimum emission potentials were observed in late summer and early autumn. The emission potentials, both conventional evaporation –based potential and more complex hybrid emission potential, were almost an order of magnitude higher in winter when compared to those measured during the second half of growing season. Interestingly, there was remarkable day-to-day variation in emission potential in spring, when the trees are recovering from wintertime dormancy (see Aalto et al., 2015).

The maximum in the emission potential of current year shoots was observed in spring (see Aalto et al., 2014), at the time of growth onset, whereas the emission potential of 2-year old pine shoots was increasing towards autumn. The common feature of monoterpene emissions during the emission potential maxima was that temperature alone was unable to explain the variation in emission rates.
CONCLUSIONS

The results strongly suggest that applying constant emission capacity in VOC emission modeling will likely result in significant, season-related biases in emission estimates, and that needle age classes clearly differ both in emission potentials and in features related to seasonality. If these features are not taken into account in modeling the production of precursors for atmospheric secondary aerosol formation, it will likely lead to significantly biased results.

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INTRODUCTION

Ambient air greenhouse gas (GHG) concentration measurements can be performed on wet or dried sample. Since the water vapour in the atmosphere has a high variability, the dilution effect makes the comparison of the GHG concentrations in wet air meaningless. Thus, if the GHG measurements are performed on wet sample, for the world-wide uniformity, the mole fractions have to be extrapolated to dry-gas conditions. The other reason for correcting the wet results refers to the measurement techniques. Many measurement techniques suffer from significant interference from water vapour. Picarro G1301, G2301 and G2401 analysers fulfil the requirements for ICOS atmospheric stations for CO$_2$ and CH$_4$ measurements (ICOS Atmospheric Station Specifications). All these analysers correct the wet results, but the correction factors determined by the manufacturer need to be improved by reassessing the factors (Rella et al., 2013).

For a proper assessment of the water vapour correction factors, the analyser has to be supplied with sample air with constant CO$_2$ and CH$_4$ mixing ratios containing differing but stable water vapour concentrations at a range of the ambient air, as well as dry air for the reference. In principle, the test is not difficult to perform, but commercial instruments producing several stable water vapour concentration levels are not easily available. Thus, ICOS Atmospheric Thematic Centre built a system for water vapour correction assessment from commercial components. The system is shown to fulfil the requirements of stability and reproducibility and is now a part of routine equipment.

So called “water droplet method” is easier and more suitable method for water vapour correction assessment in the field conditions; it is simply based on humidifying a dry gas stream by adding a droplet of water in the sample line and letting it dry. The equipment needed for this test are simple and cheap, and it is possible to carry out the test within a few hours; however, the outcome using the water droplet method is not as accurate.

The mobile laboratory (MobileLab) of the ICOS Atmospheric Thematic Centre, a quality control unit of the ICOS atmospheric station network, is now performing the water vapour correction assessment as a part of the audit visits for atmospheric stations.

INSTRUMENTATION

Air flow with stable water concentrations is essential for successful water vapour correction assessment, as already mentioned. In the new test setup stable water concentration is produced with a self-built instrument from components manufactured by Bronkhorst High-Tech B.V. The main part of the instrument is Controlled Evaporator Mixer (CEM), which mixes water and dry air flows it is supplied with. Both flows are controlled by mass flow controllers (MFCs). The water flow from the reservoir to the CEM is generated by pressurising the reservoir headspace with a gas free of CO$_2$ and CH$_4$ (e.g. N$_2$, He, ...
synthetic air). Since the MFC for water is very sensitive to air bubbles, helium is recommended for the pressurisation due its low water solubility. To enable very low water flows (down to 0.1 g/h), the MFC for water is based on Coriolis type mass flow sensor and is thus extremely sensitive to vibration. Air flow for the CEM is taken from a gas cylinder filled with dried ambient air. To achieve stable mixing of water to air, the sample flow has to be 1.5–2 l/min – clearly higher than required for the instrument inlet flow (sample flow for Picarro G2301 and G2401 is less than 0.3 l/min). The high air flow is also needed to produce sample air with low water concentrations, since the MFC for water is not reliable with the water flows below 0.2–0.3 g/h. To avoid water condensation on the walls of the CEM-system and the tubing, all the parts from the mixer to analyser inlet port are heated.

WATER VAPOUR CORRECTION ASSESSMENT DURING AUDIT

The MobileLab is equipped with a Picarro G2401 and performs a water vapour correction assessment for the analyser during each station audit. The assessment will be made also for the local analyser at least once during the audit. Each ICOS atmospheric station’s instrument should have been performance tested by ICOS ATC Metrology Laboratory, which also includes water vapour correction assessment with similar CEM-system. Thus, the test made during audit by the MobileLab is comparable with the initial test made by Metrology Laboratory. The MobileLab will also ensure that the local personnel of the atmospheric station is capable to perform so called “droplet test” for the analyser regularly, about once a year, as a quick test for the analyser status.

As the water concentration for the assessment should be covering ambient range at the station, the typical test concentration range is from 0 to 3.5 % (mol/mol) of water vapour in air (Figure 1), which cover the main concentrations the analysers face at the European measurement stations. If, due to the location, the station’s ambient air water concentration has an unusual range, the test conditions have to be adapted to represent the local conditions better.

Figure 1. Typical water concentrations during the assessment of water vapour correction factors including the dry air measurements before and after the water addition.
The water vapour correction factors (a, b) are determined by fitting a second order equation (1) to the drawdown of the analyser gas concentration reading (Rella et al., 2013).

\[
\frac{c^{(wet)}}{c^{(dry)}} = 1 + aH + bH^2
\]  

(1)

where H is the water concentration reported by the instrument. The correction factors have to be determined for each individual analyser, and reassessed with ageing of the analyser. Also the correctness of the default correction factors, determined by the manufacturer, may change from analyser to analyser. In figure 2 are shown water vapour correction assessment performed for a Picarro G2401 analyser, for which default water vapour correction was improved substantially by the manually assessed correction factors. Picarro G2401 analyser measures also CO, and also it can be corrected with the factors determined by the CEM-system. However, the correction is more complicated to perform (Chen et al., 2013), and due to the noise of the CO signal, the correction outcome is not as essential as for the CO₂ and CH₄ concentrations.

Figure 2. The CO₂ and CH₄ concentrations of wet air measurements corrected to dry mole fractions in terms of sample air water vapour concentration. Green symbols show the concentrations corrected by the analyser default factors and red symbols when the correction factors were determined manually by the CEM-system.
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ROLE OF TANNINS IN CARBON AND NITROGEN CYCLING OF BOREAL FOREST SOIL

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Keywords: TANNIN, NITROGEN, BOREAL, SOIL.

INTRODUCTION

Soil organic matter (SOM) of boreal and arctic ecosystems account for half of the global C stored in soil and litter (Pan et al. 2011). This enormous C pool have the potential to become C source under the projected global climate change (IPCC, 2013). Ecosystem processes associated with C cycle are constrained by C and N interactions. To predict long-term soil C storage and climate feedbacks, we need profound understanding of dynamics and drivers of SOM decomposition.

In boreal forest soils, SOM content is very high and it is rich in phenolic plant secondary compounds, especially tannins. These polyphenolics have high potential to directly interfere with organic N availability through formation of recalcitrant complexes with proteins (Hagerman, 2013), and other organic N compounds, like arginine, chitin and polyamines (Adamczyk et al. 2011). High content of tannins in boreal forest soils may partially account for phenomena of soil organic N recalcitrance. To improve N uptake, also from less-available pools, plant species form intimate symbioses with mycorrhizal fungi which are capable of degrading and taking up inorganic and organic N and sharing obtained N with plant host (Heinonsalo et al. 2015). In boreal forest ecosystem ericoid shrubs form symbioses with ericoid mycorrhizal (ERM) fungi and trees form symbiosis with ectomycorrhizal (ECM) fungi (Read, 1996). Boreal forest floor is covered with ericoid plants and in soil, ECM and ERM plant roots and fungal hyphae are intermixed. Some ERM and ECM fungi have been shown to be able to take up N from recalcitrant tannin-N complexes. It was suggested that ERM plants may reduce availability of N to other plants through formation of recalcitrant organic matter, which contains protein-phenol complexes (Read, 1996; Clemmensen et al. 2013). As tannins interfere also with enzymes (e.g. Adamczyk et al. 2011), their influence on SOM decomposition and N uptake by mycorrhizal plants seems to be very complex. Moreover, it is predicted that climate change induce higher production of tannins or production of more reactive tannins (e.g. Tharayil, 2011). Thus the role of tannins in boreal forest soil nutrient cycling may increase in the future. The aim of the study was to show how mycorrhizal plants affects SOM decomposition in polyphenolic-rich ecosystem.

METHODS

Soil for this study was collected in the vicinity of SMEAR II station of Helsinki University at Hyytiälä (61°84'N, 24°26'E) in southern Finland The soil was haplic podzol and Scots pine (Pinus sylvestris L.) was the dominating tree species. Soil was taken from the organic layer and placed in mesh bags with different mesh size to form 3 types of treatment: mesh size 1 mm do not limit fine root and hyphal in-growth, 50µm mesh exclude roots but not fungal hyphae and 1µm excludes also fungal penetration (Wallander et al. 2011). Mesh bags in 24 replicates per treatment (1µm, 50µm, 1mm) were placed in humus layer at Hyytiälä station in May 2013. We studied N pools from mesh bags after 1, 2, or 3 years of incubation at field experiment. We measured different N pools, activities of organic matter degradation related enzymes (Pritsch et al. 2011) and content of tannins (acid-butanol assay (Hagerman, 2013)) as well as nitrogen pools including inorganic N (ammonium and nitrate), total free amino acids, degradable and recalcitrant N (acid hydrolysis) (Kieloaho et al. 2016).
RESULTS AND DISCUSSION

Soil organic matter in mesh bags underwent substantial changes during the three year incubation in boreal forest humus layer. Amount of inorganic N was substantially decreasing, however, the level of condensed tannins was on the same level during the experiment, and in 1mm treatment fine roots were providing even more tannins with time. The results suggests that mycorrhizal plants build up recalcitrant SOM using root-derived tannins. We propose that turnover rate of plant roots with high CT content is crucial for SOM quality and quantity. However, the high CT content does not seem to be hindering the SOM decomposition (data not shown), indicating the root-associated microbiota has the ability to access C and nutrients from tannin-rich SOM. Such plant-soil interaction may constrain predicted increase of CO₂ production from soil through formation of recalcitrant SOM and by-passing organic matter mineralization. This study underlines that plant-soil feedbacks and especially soil chemistry behind this interaction are decisive factors for magnitude of CO₂ release from SOM.

Figure 1. Condensed tannins in mesh bags. Statistical significances (p<0.05) between the different treatments within the sampling year is marked with *, Statistical significances (p<0.05) between the different sampling years within the treatment is marked with capital letters.

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THE FIRST SEASON OF EDDY-COVARIANCE MEASUREMENTS IN MUKHRINO STATION, WEST SIBERIA

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KEYWORDS: WEST SIBERIA, MIDDLE TAIGA, PEATLAND ECOLOGY, CARBON DIOXIDE FLUX, EDDY-COVARIANCE.

INTRODUCTION

Wetlands represent an important component of the global carbon cycle, being a significant course and sink of carbonaceous compounds. High sensitivity to climate change imparts instability to the carbon and energy cycling in peatlands. Siberian peatlands, due to their size and location in the region of pronounced future changes, therefore pose one of the biggest unknowns in the world climate.

Despite the equivocal agreement on the high importance of Boreal wetlands for the biospheric and atmospheric processes (Smith et al., 2004; Sheng et al., 2004) detailed studies involving state-of-art techniques remain scarce in this region. This is mainly due to the lack of developed measurement sites with the infrastructure suitable for continuous monitoring of the ecosystem-atmosphere exchange processes, and frequent inaccessibility of key ecological zones and biomes. West Siberian peatlands, in particular, have not been investigated using the modern measurement techniques.

This study was motivated by the need and interest to fill the Siberian observational gap by establishing the eddy-covariance (EC) measurement setup in a typical West Siberian peatland. The objective of the project was to construct a dataset characterizing the surface exchange of carbon and energy that would be compatible with the estimates made in other peatlands.

SITE DESCRIPTION

Mukhrino Field Station (MFS) in the center of Western Siberia (Khantry-Mansiysk Autonomous District, Russia, http://mukhrinostation.wordpress.com) was established as a part of the UNESCO chair “Environmental Dynamics and Global Climate Change” of Yugra State University in 2009. MFS is located in a mixed forest/floodplain/peatland landscape 30 km South-west from the city of Khantry-Mansiysk (60°53’ N; 68°42’ E) on the left terrace of the Irtysh river (Figure 1).

The research activities at MFS are conducted, firstly, in peatland, and, secondly, in Irtysh floodplain. The peatland site is representative of the pristine carbon-accumulating mire ecosystems of the West Siberian Middle taiga zone. These mires cover about 60 % of the land surface of this zone, and are mainly represented by the oligotrophic rain-fed variety, bogs. Also, native old dark coniferous and mixed forests, as well as wetland and meadow graminoid vegetation in vast flood plains of Irtysh and Ob rivers are represented. The immediate vicinity of the measurement setup (the eddy-covariance footprint area) presents a complex mosaic of typical raised bog surfaces covers (hollow-hummock complexes, flarks and ponds). The hummocks are sparsely populated by pine trees ranging between 1-4 m in height. These features are found in a large proportion of the regional mires.
Figure 1. (a) map showing the Mukhrino station location, (b) satellite photo (Digital Globe, CNES/Astrium) with footprint estimates superimposed, (c) photo of the EC tower, facing southwest. The red cross in (a) and (b) marks the location of the EC tower. The isolines in (b) delineate the 70% cumulative source zone in the three stability classes. The black areas are inundated hollows/ponds, brown areas are open peat carpets, and green areas are pine-covered strings/hummocks.

MATERIALS AND METHODS

Automatic weather station provides many parameters both in a wet hollow and in a pine-dwarf shrub-sphagnum ecosystem of oligotrophic mire, including air and soil temperature profiles, air and soil moisture, solar radiation (direct and reflected), wind speed and direction, precipitation, atmospheric pressure. Eddy-covariance (EC) measurements were launched in April 2014. Currently, the EC system consists of a LI-7500 gas analyzer and a Gill R3 anemometer, providing the estimates of CO₂ and energy fluxes, and will be expanded with methane analyzer in near future. Data processing and quality control are done in full compliance with the accepted routines; eddy-covariance data is analyzed with the EddyUH software (Mammarella et al. 2016). No similar measurements have been brought out anywhere else in the West-Siberian region; the nearest stations with equivalent setup are located approx. 1000 km to the East and South-East.

The CO₂ component fluxes, respiration (Re) and gross primary productivity (GPP) were modeled and gapfilled using mainly standard approaches. Re (μmol CO₂ m⁻² s⁻¹) was modeled based on nighttime data, yielding the relation
\[ R_e = 0.8 \times 2.3^{\left(\frac{T_a - T_{net}}{10}\right)} \]. A more novel approach was used to gapfill GPP. A Michaelis-Menthen model

\[ GPP = \frac{P_{max} \times PAR}{k + PAR} \]

was fit to the data in a 30-day moving window, after which the resulting daily parameter values of \( P_{max} \) and \( k \) were spline-interpolated back to the 30-min resolution of the original data.

RESULTS AND DISCUSSION

Eddy-covariance and meteorological parameters were obtained at the station in May-August 2015. The measurements were continuous, having some of gaps resulting from technical malfunctions and lack of energy at night. The energy balance was closed to 90\%, indicating high quality of the data (Fig. 2).

Figure 2. Energy balance closure. Ground heat flux is modeled from soil temperature profile.

The site Bowen ratio (\( \beta = \) sensible/latent heat flux) was low for this peatland type (0.3) and very stable seasonally. Its low value may be, at least partly, explained by unusually high wetness and precipitation in summer-2015. Five significant rain episodes kept the water table high, but cloudiness also resulted in low photosynthetically active radiation, high relative humidity and low air and soil temperatures (Figure 2).

Maybe not completely as expected, moist and cool conditions of 2015 allowed for high uptake at low respiration, resulting in high net ecosystem exchange (NEE). The largest carbon uptake was measured in June and July (-74 and -78 gC m\(^{-2}\), respectively), while in May the cumulative sum of NEE was -47 gC m\(^{-2}\). The May-August cumulative NEE of -224 gC/m\(^2\) (decomposing into 151 gC/m\(^2\) of respiration and -375 gC/m\(^2\) of gross primary productivity) (Fig. 3) lies within the literature values for similar ecosystems, but approaches the highest observations. In comparison, NEE of the same period in a dry year of 2016 was almost twice lower (not shown), pointing at the importance of the water availability control for the ecosystem.
Figure 2. Time series of the environmental drivers. The grey dots are 30 min measurements, while the black lines represent daily averages except in (d), where it shows the cumulative precipitation.

Figure 3. (a) Seasonal variation of NEE measured with the eddy-covariance system; the grey dots correspond to 30 min averages and the black line to the daily averages. (b) Cumulative sums of NEE, Re and GPP. The data are gap-filled.

CONCLUSIONS

Meteorological variables, surface fluxes of CO₂ and energy were for the first time measured with the eddy-covariance technique in a West Siberian bog. High quality data was obtained, which allowed for extensive analyses of the surface exchange processes and their controls. The measurement year 2015 was rainy and wet, which might have resulted in an unusually high net uptake, as the comparison with dry 2016 suggests. The investigations will
be continued in future, with the aims of better understanding of interannual variability of greenhouse gas and energy exchange and assessing the complete carbon budget (including CH₄).

REFERENCES


INTRODUCTION

Human impact on the increase of the atmospheric pollutants globally has resulted in changes in Arctic and Antarctic ecosystems and climate which has been demonstrated to be crucial for the fragile ecosystems of these regions (e.g. Vaughan, 2006). The latest IPCC report states (IPCC, 2013): “Over the last two decades, the Greenland and Antarctic ice sheets have been losing mass, glaciers have continued to shrink almost worldwide, and Arctic sea ice and Northern Hemisphere spring snow cover have continued to decrease in extent (high confidence)”. Atmospheric aerosol particles are an integral part of the climate, having effects on water-, carbon-, and nutrient cycles, the amount of solar radiation entering the surface and changing the amount of cloudiness and rain, as well as the properties of clouds. These effects are now reflected also on the previously pristine Antarctica.

Globally, aerosol particles cool the climate by direct scattering of solar radiation and via their impact on cloud radiative properties. On snow and ice -covered regions the clouds may however induce a positive climate forcing; increasing the aerosols can in fact enhance warming of the surface (Mauritsen et al., 2011). There is also some evidence that at pristine polar regions the aerosol-cloud feedback can be extremely sensitive to aerosol numbers (Asmi et al., 2012). In polar regions of particular importance is also the snow and ice albedo reduction by black carbon (BC) and organics containing particles which can influence snow coverage by warming the atmosphere, reducing surface-incident solar energy, and reducing snow reflectance after deposition (AMAP, 2011).

Southern Ocean is the main source of natural sea spray, sulphate and organic aerosols in Antarctica (e.g. Virkkula et al., 2006; Asmi et al, 2010). Also secondary aerosol sources are significant in summer season, but have been evidenced to occur also in full-darkness winters (Asmi et al., 2010; Järvinen et al., 2013). Further to this, absorbing black carbon, an indication of anthropogenic influences, is found on different sides in Antarctica, having a decreasing concentration gradient from coast to the central Antarctic (Weller et al., 2013). Recent studies made in east-Antarctica have shown an inter-annual cycle of absorbing aerosols with sources mainly attributed to long-range transport from South-American biomass burning (Fiebig et al., 2009; Weller et al., 2013). The sole comprehensive black carbon characterization made previously in Antarctic Peninsula, further isolated South-America as a major anthropogenic aerosol source (Pereira et al., 2006). However, also the increasing tourism, traffic and settlements within the Antarctica cause unknown contribution to the current aerosol budgets which have not been largely studied by now.

To understand the inter-annual characteristics of the aerosol particles in Antarctic Peninsula current climate, their sources and interactions, we studied the particle chemical and optical properties continuously during three consecutive years. Measurements were made using semi-automated instrumentation in Argentinean station Marambio (64°14’S 56°37’W). The main scientific questions are: 1) How are aerosol radiative properties and which compounds are responsible for these?, 2) What are the main sources of aerosols on different seasons, and 3) How much aerosols can be traced to arise from anthropogenic activities?
METHODS

Measurements were started in February 2013 and continued year-round in a clean-air laboratory installed about 400 m from upwind from the station main sources. Particle chemistry PM2.5 and PM10 fractions were studied with weekly collection of filter samples using a virtual impactor (VI). Laboratory analysis and chemical mass balance were calculated as in Asmi et al., 2010. Particle optical properties were measured with an Aurora 3-wavelength nephelometer (scattering) and with a multi-angle absorption photometer (absorption), both with 5-min time resolution. Nephelometer data was corrected as suggested by Müller et al., 2011.

Air mass back trajectories at arrival levels of 500 m a.s.l. for Marambio were calculated using a HYSPLIT 4 model (Draxler and Hess, 1997, 1998). The National Weather Service’s National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS) was used as a meteorological data input for the HYSPLIT model runs and a new trajectory was started every 3 h calculating 120 h backwards.

CONCLUSIONS

Aerosol chemistry shows a distinct seasonal pattern (Figure 1). Winter aerosol is mainly composed of sea salt, while in summer the marine emissions of sulphate and methanesulphonic acid (MSA) add to the chemistry. These compounds, in addition to organics, are also likely to contribute to secondary particle formation and growth during summer. Total aerosol mass is slightly higher in winter, likely due to more stormy weather which increases the marine primary emissions.

Absorbing aerosols in Marambio do not, in contrast to previous studies from Antarctica, show any clear inter-annual cycle (Figure 2). The annual average BC was around 10 ng m\(^{-3}\), similar to previously reported 8.3 ng m\(^{-3}\) in Peninsula (Pereira et al., 2006). Interestingly, no clear distinction between air mass origin for low and high BC concentrations was found, and thereby, we may not conclude on the impact of biomass burning as a strong factor in accordance with previous studies. The only correlation for BC, as well as for scattering aerosol, was found with wind speed. Thereby, the primary release mechanisms and cryosphere-atmosphere interactions appear to play a more significant role than previously thought for Antarctic aerosol load.

To our knowledge, this is the first such long-time comprehensive aerosol particle characterization made at the region of Antarctic peninsula. The results explain more specifically which factors are responsible for the aerosol particle climatic impacts year-round in the peninsula region and which are the main drivers.
Figure 2. Monthly median (with quartiles) and averaged (red dots) black carbon mass concentration in Marambio, measured during 2013-2015.

ACKNOWLEDGEMENTS

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REFERENCES


UPSCALING CHLOROPHYLL FLUORESCENCE FROM THE FOREST TO THE SATELLITE PIXEL

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Keywords: GROSS PRIMARY PRODUCTIVITY, SOLAR-INDUCED CHLOROPHYLL FLUORESCENCE.

INTRODUCTION

The retrieval of solar-induced chlorophyll fluorescence (SIF) from space has the potential to revolutionise remote sensing of terrestrial primary productivity. This is because the SIF signal, which originates from deep within the photosynthetic machinery, is intricately connected to the efficiency of photosynthesis (Porcar-Castell et al., 2014).

Both SIF and more traditional reflectance index based algorithms typically utilise the light use efficiency model (Monteith and Moss, 1977) to estimate Gross Primary Productivity (GPP) from space:

$$GPP = \epsilon \times fPAR \times PAR$$ (1)

where PAR is photosynthetically active radiation incident on the canopy, fPAR is the fraction of PAR that is absorbed by the canopy and $\epsilon$ is the efficiency at which absorbed PAR is converted into sugars; $\epsilon$ is representative of all those processes that suppress photosynthesis such as water or heat stress. Broadband reflectance indices (e.g. NDVI, EVI) can be used to estimate fPAR only; additional information, usually from meteorological re-analyses, is required for the prediction of GPP. In contrast, SIF contains information relating to both $\epsilon$ and the amount of light absorbed by the canopy ($APAR$, where $APAR = fPAR \times PAR$). Accordingly, a linear relationship between monthly averaged point measurements of GPP (using the eddy covariance technique) and co-located SIF retrievals has been observed for crops (Guanter et al., 2014). Similar results have also been observed for the boreal forest (Walther et al., 2015).

The fact that there is a strong relationship between GPP and SIF for the boreal forest is promising, especially as Peltoniemi et al. (2015) have shown that reflectance based algorithms likely over-predict GPP in the Finnish boreal forest. However, more work is required to understand the mechanisms behind the relationships. At our field site, we have the instrumentation required to delve deeper into these mechanisms. Pertinent questions include:

1. Do changes in SIF relate to reductions in $\epsilon$ at the canopy scale?
2. What is driving the spring recovery dynamics of SIF?
3. What role does the understory play in the SIF signal?

By rigorously validating satellite SIF retrievals with data from the SMEARII research station (Finland) we aim to address the above questions.
METHODS

SIF retrievals from GOME-2 were produced according to Köhler et al. (2015). SIF time series were extracted from a pixel co-located at SMEARII research station and smoothed using a Savitzky Golay filter. Leaf level fluorescence yields ($\Phi_f$) were estimated from a monitoring Pulse Amplitude fluorescence (MONIPAM) system and GPP fluxes were estimated using the eddy covariance technique.

CONCLUSIONS

For the most part, the SIF signal tracks GPP (figure 1). The yield of pine needle fluorescence ($\Phi_f$) follows a different seasonal course to SIF. This is partly explained by the dependency of SIF on PAR, as SIF is a function of both $\Phi_f$ and PAR. Divergence between $\Phi_f$ and SIF could also relate to changes in canopy iPAR; a potential mechanism being the additional fluorescence contribution to SIF from the understory.

Figure 1: Time-series of measurements at SMEARII station. GPP (top), co-located GOME-2 SIF retrieval (middle) and yield of chlorophyll fluorescence from MONIPAM (bottom). For SIF grey squares are raw retrievals and red line is filtered estimate.
ACKNOWLEDGEMENTS

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REFERENCES


A new computational approach to generate footprints for urban flux and concentration measurements via large-eddy simulation

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Keywords: Large-eddy simulation, footprint, urban micrometeorology, eddy-covariance.

INTRODUCTION

In the context of flux and concentration measurements in micrometeorology, the footprint is a concept used to describe the surface area that contains the sources (and sinks) which contribute to the measured signal. In another words, it is the 'field of view' of a given sensor whose identification is essential in interpreting the obtained flux or concentration values in their correct spatial extent. Mathematically, the footprint is a transfer function, which relates the value of a measurement $\eta$ at location $x_M$ to the spatial distribution of flux or concentration sources $Q$ from a volumetric domain $\Omega$ of interest:

$$\eta(x_M) = \int_{\Omega} Q(x') f(x_M, x') \, dx'.$$

Thus, effectively the footprint acts as a spatial weighting function for the sources. Explicit analytical expressions have been derived for the footprint functions (Schmid, 2002), but only under the assumptions that (1) steady-state conditions prevail during the analyzed period, (2) turbulent fluctuations in the atmospheric boundary layer (ABL) are horizontally homogeneous, and (3) there is no vertical advection (Aubinet et. al., 2012). But in urban environments, where the ABL flows are characterized by strong heterogeneity, assumption (2) becomes strictly invalid and assumption (3) highly questionable. This renders the use of analytical footprint models questionable in urban studies, motivating the search for new, generally applicable techniques to generate footprints.

The most promising approach to evaluate footprints in arbitrarily heterogeneous areas combines Lagrangian stochastic (LS) particle model with large-eddy simulation (LES) technique (Steinfeld et. al., 2008 and Hellsten et. al., 2015). LES refers to an approach in computational fluid dynamics where the Navier-Stokes equations are solved on a sufficiently refined grid, which allows the energy containing turbulent structures (large eddies) to be time-accurately resolved while employing a subgrid-scale model to account for the effect of the small energy dissipating eddies. The coupling of LS with LES (LES-LS) refers to an approach where trajectories of passive weightless particles are simultaneously solved with the flow field. To account for the stochastic nature of the sub-grid-scale turbulence, the time evolution of the particles is solved utilizing velocity fields that contain both deterministic (resolved) and stochastic contributions. Although both LES and LS approaches require considerable computational resources, their coupling provides the most accurate, widely applicable, and reliable means to study footprints in ABL flows.

The objective of this development effort is to device a LES-LS based methodology that enables the generation of detailed footprints for eddy-covariance (EC) sensor sites placed in complex urban surroundings. The case study is staged in downtown area of Helsinki, the coastal capital city of Finland, and focuses on the EC sensor that is mounted on the roof of a centrally located Hotel Torni building.
Incidentally, determining a footprint for such roof-mounted sensors is associated with complications which must be carefully accounted for by the developed methodology.

METHODS

In this study the parallelized large-eddy model, PALM (Maronga et. al., 2015), is used to run the coupled LES-LS 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 well suited for the current study since it has been carefully optimized for massively parallel computing.

The topography model of Helsinki for the LES simulation has been constructed from laser-scanned data at 2 m resolution and comprises of a 4 km by 2 km land area from downtown region. See Figure 1 for a three-dimensional illustration of the LES model's topography. To ensure that the flow behavior between the buildings and within the street canyons is captured accurately, a uniform spatial resolution of 1 m was specified for the LES grid. Considering the size of the computational domain \( \max(x) = 4096 \text{ m}, \max(y) = 2048 \text{ m}, \text{ and } \max(z) = 512 \text{ m} \) the LES model becomes exceptionally large, containing over 4 billion grid points. Urban LES simulations at this scale and accuracy have not been reported before.

The meteorological conditions for the simulation were adopted from September 9\textsuperscript{th} in 2012 when south-westerly wind and near neutral ABL conditions were recorded. The boundary layer height (obtained from Lidar data) of 300 m was fixed by specifying a mean potential temperature profile with a strong inversion layer. Physically meaningful inlet boundary conditions were generated by recycling the solution from yz-plane at \( x = 1024 \text{ m} \) back to the inlet. For this reason, the first half of the computation domain \( (0 < x < 2 \text{ km}) \) features flat terrain. To reduce the computational time required to reach statistically stationary conditions, the urban simulation was initialized with a pre-computed ABL solution over a flat surface.

The particles for the LS model are seeded 1 m above the topography and released at 10 s intervals. Those particles that hit a target volume \( \Omega_T \), set around Hotel Torni’s measurement site, are sampled and their coordinates of origin and incident velocity data recorded. The target volume has to be adequately sized in order to accumulate a sufficiently large number of particle hits during a 2-3 h simulation. The

Figure 1: Three-dimensional overview of Helsinki LES model's topography. (T) indicates the Hotel Torni EC-measurement site.
recorded particle hits yield a dataset \( \mathcal{S} \), which is subsequently divided into a series of subsets \( \mathcal{S}_{i,j,k} \) (s.t. \( \mathcal{S} = \bigcup_{i,j,k} \mathcal{S}_{i,j,k} \)) each containing the record obtained from a target subvolume \( \Delta \Omega_{\text{t},i,j,k} \). The division of the target volume into \( n_x \times n_y \times n_z \) subvolumes follows a structured Cartesian discretization. This procedure enables a systematic piecewise post-processing of independently mean-flow corrected footprint functions \( f_{i,j,k} \) which locally adapt to the variable wind conditions just above the Hotel Torni building.

The obtained series of partially converged sectional footprints \( f_{i,j,k} \) are subjected to a spatial sensitivity study whose purpose is to identify which sectional footprint contributions can be utilized in the selective assembly of the final result

\[
f = \frac{\sum_{i,j,k \in \mathcal{K}} D_{i,j,k} f_{i,j,k}}{\sum_{i,j,k \in \mathcal{K}} D_{i,j,k}}
\]

where \( \mathcal{K} \) is the set of all \( i, j, k \) combinations which have been selected via sensitivity analysis and \( D_{i,j,k} \) refers to the denominator used in computing the corresponding \( f_{i,j,k} \).

The Helsinki LES-LS simulation was computed on the Cray XC-40 supercomputer of the IT-Center of Science (CSC Oy) utilizing 2048 CPUs. The simulation was run for three hours of physical time, during which over \( 19 \times 10^6 \) Lagrangian particles were recorded at Hotel Torni's target. The piecewise post-processing of the footprint was carried out with different target volume discretizations and the results were compared to analytical footprint model by Korman and Meixner (2001).

CONCLUSIONS

The developed methodology that combines high-resolution LES-LS simulation with a new piecewise post-processing strategy is shown to be a robust approach to construct detailed footprints for urban flux and concentration measurements. Figure 2 illustrates a comparison between an analytical footprint and a LES-LS footprint, which is selectively assembled from an initial set of \( 3 \times 5 \times 3 \) sectional footprints. The LES-LS footprint reveals in striking detail how the urban terrain may influence the footprint distribution. For instance, an order of magnitude difference in source weights is observed between adjacent roof tops and street canyons. A subsequent analysis of the results uncovers that the use of analytical footprints in urban measurement campaigns may become a significant source of error and uncertainty in the spatial interpretation of EC measurements.

Figure 2: Comparison of the LES-LS generated footprint (left) and an analytical Korman-Meixner footprint (right). The results are normalized to yield identical global integrals.
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REFERENCES


SENSITIVITY ANALYSIS OF A METEOROLOGICAL PRE-PROCESSOR USING
ALGORITHMIC DIFFERENTIATION

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Keywords: METEOROLOGICAL PRE-PROCESSOR, MONIN-OBUKHOV SIMILARITY, ALGORITHMIC DIFFERENTIATION, SENSITIVITY ANALYSIS.

INTRODUCTION

A model developed at the Finnish Meteorological Institute to model the emissions, and the dispersion and transformation of pollution from an open road network (CAR-FMI) is used for such purposes (e.g. Kukkonen et al., 2001). The model is a Gaussian finite line source model where the road network comprises the emission sources (Kukkonen et al., 2001). Like any short-range urban dispersion model, CAR-FMI requires that information about the state of the atmospheric boundary layer is provided to it externally. This information is generated by a meteorological pre-processor MPP-FMI (Karppinen et al., 1997, 2000), which uses basic meteorological observations to derive the necessary quantities describing the atmospheric state required by CAR-FMI. These evaluations are done by applying an energy-flux method that estimates turbulent heat and momentum fluxes in the boundary layer.

MPP-FMI is based on the work by (Van Ulden and Holtslag, 1985) with modifications that makes the parametrisation more suitable for high latitudes. The core of the method is the surface heat budget equation

\begin{equation}
Q^* - Q_G = Q_H + Q_E.
\end{equation}

In Eq. (1), $Q^*$ is the surface net radiation, $Q_G$ is the soil heat flux, $Q_H$ is the sensible heat flux, and $Q_E$ is the latent heat flux.

First, the pre-processor estimates the sign of the $Q_H$ by decomposing the surface heat budget equation into components. This determines if the subsequent calculations are performed using stability functions for stable or unstable conditions (Karppinen et al., 1997, 2000). Initially, $Q^*$ is broken into short-wave and long-wave components. Latent heat flux ($Q_E$) is estimated using a empirical saturation enthalpy curve as a function of temperature and a estimated ground moisture parameter from meteorological data. Furthermore, the friction velocity ($u^*$) is also first estimated without stability functions since the stability is not yet known. Depending on the atmospheric stability, different stability profiles are used for $u^*$ and temperature scale ($\theta^*$). Then, through iteration, the Obukhov length ($L$) is changed. During the iterations, the temperature scale is calculated using stability profiles and using the estimated $Q_H$ obtained during the iteration. The iteration stops when these two temperature scales match.

The sensitivity of this meteorological pre-processor has not previously been investigated, which is the focus of this work. The sensitivity analysis of the pre-processor parametrisation is studied using an algorithmic differentiation tool called TAPENADE (Hascoet and Pascual, 2013). The differentiated code will, in addition to the original output, also yield the partial derivatives of the output. The sensitivity of the energy-flux method is of interest because we want to evaluate the performance of the pre-processor, and investigate its sensitivity to the input data, in order to find ways in which it can be improved.
Algorithmic differentiation (AD) is a branch of computer science that deals with the numerical evaluation of derivatives of functions that are implemented in a computer programme, in this case MPP-FMI. Any computer program, no matter how complex, performs a sequence of arithmetic operations (+,-,\ldots) or elementary functions (\exp, \sin, \log, \ldots) whose derivatives are known. AD exploits this fact by applying the chain rule of differentiation to the entire sequence of operations within the program (Griewank and Walther, 2008). This systematic approach yields numerical derivative values at machine-precision, which describe how the program's results (i.e. outputs) depend on its input parameters. It is important to note that AD carries out each differentiation operation exactly and does not employ approximate techniques involving finite differences. For this reason AD does not suffer from truncation or round-off errors.

AD is further separated into two modes, a forward mode or a reverse mode (Griewank and Walther, 2008). Here the discussion will be limited to the forward mode, which has been employed in this study. As a starting point, consider an arbitrary computer program that takes \( n \) input variables and returns \( m \) outputs. It can be described as a vector-valued function

\[
y = F(x) \tag{2}
\]

such that, the function \( F \) maps \( \mathbb{R}^n \to \mathbb{R}^m \) where \( x \in \mathbb{R}^n \) defines the input and \( y \in \mathbb{R}^m \) the output vectors. Application of the forward mode AD to (2) yields a new implementation of the program, which, in addition to the original function evaluation, evaluates its differential

\[
\dot{y}_k = F'(x) \dot{x}_k \tag{3}
\]

where \( F'(x) \in \mathbb{R}^{m \times n} \) defines the Jacobian matrix, which contains the all first-order partial derivatives \( \frac{\partial y}{\partial x} \) and \( \dot{x}_k = (\frac{\partial x_1}{\partial x_k}, \frac{\partial x_2}{\partial x_k}, \ldots, \frac{\partial x_n}{\partial x_k})^T \) is the seeding vector, which can be viewed as the \( k \)th unit vector that operates on the Jacobian. The result is the \( k \)th column from the Jacobian matrix \( \dot{y}_k = (\frac{\partial y_1}{\partial x_k}, \frac{\partial y_2}{\partial x_k}, \ldots, \frac{\partial y_m}{\partial x_k})^T \) which yields the dependency of all outputs with respect to the user-specified \( x_k \) input parameter. In the forward mode differentiated computer program, the chain rule-based derivative evaluations contained in Eq. (3) are carried out following the same order as the associated operations in Eq. (2), but always such that the derivative operations are executed after their corresponding step in the original program have completed.

A typical goal in sensitivity analysis is to obtain the full Jacobian. Utilizing forward mode AD, this is achieved by repeating the computation of Eq. (3) \( n \) times to yield all the columns from the Jacobian matrix. This is best illustrated with an example matrix (Eq. 4) where the first column of the Jacobian is chosen. Thus, for a given input \( x \) one can construct the Jacobian using AD and extract the derivatives of the output of interest at that point. This procedure can then be repeated for any number of points.

\[
\dot{y}_1 = \begin{bmatrix}
\frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} & \ldots & \frac{\partial y_1}{\partial x_n} \\
\frac{\partial y_2}{\partial x_1} & \frac{\partial y_2}{\partial x_2} & \ldots & \frac{\partial y_2}{\partial x_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial y_m}{\partial x_1} & \frac{\partial y_m}{\partial x_2} & \ldots & \frac{\partial y_m}{\partial x_n}
\end{bmatrix} \dot{x}_k \tag{4}
\]
In this work, the differentiation was performed using the AD tool called TAPENADE (Hascoet and Pascual, 2013). TAPENADE has been developed by the French National Institute for computer science and applied mathematics (Inria) and is free of charge as an online service.

RESULTS

The meteorological pre-processor is used to estimate turbulent fluxes and atmospheric stability and makes use of routinely observed meteorological observations (Karppinen et al., 1997, 2000). These meteorological observations include temperature ($T_2$), wind speed ($U$) at 10 meters, amount of predominant clouds ($C_C$), cloud height ($C_z$), incoming short-wave solar radiation ($R_S$), and the state of the ground (wet, dry, snow, ice etc.). Additional input variables are surface roughness length ($z_0$) and a list of surface albedo ($r$) values. These input data are then used to estimate the Priestly-Taylor moisture-parameter ($\alpha$), Obukhov length ($L$), temperature scale ($\theta^*$), friction velocity ($u^*$), sensible heat flux ($Q_h$), latent heat flux ($Q_e$), surface albedo ($r$) and net radiation ($Q^*$). In addition, radiosondes are used to determine the height of the mixing layer. Here, we focus on the sensitivity of the energy-budget method implemented into MPP-FMI, which is based on the work by (Van Ulden and Holtslag, 1985) The sensitivity study was performed using artificial data for the various input variables for the pre-processor.

Outside of this work, some parameters in the MPP-FMI that are used in the calculations get their values through a table lookup. For example, precipitation and state of the ground input data are used in a table lookup to estimate a value for $\alpha$. From a sensitivity study point-of-view, it makes more intuitive sense to be able to assess the sensitivity to $\alpha$ directly rather than the sensitivity of the table lookup procedure. Therefore, in this work, the table lookup variables $r$ and $\alpha$ are included as inputs to the MPP-FMI which reduces the number of input variables to be analysed. Therefore, this sensitivity study becomes more straightforward to interpret because inherent step-functions of a table lookup is avoided. Table 1 summarises the range of input variables that was used in the sensitivity study.

<table>
<thead>
<tr>
<th>Inputs</th>
<th>$z_0$</th>
<th>$r$</th>
<th>$T_2$[C]</th>
<th>$C_C$</th>
<th>$C_z$[m]</th>
<th>$U$[m/s]</th>
<th>$\alpha$</th>
<th>$R_S$[Wm$^{-2}$]</th>
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<tbody>
<tr>
<td>Range</td>
<td>0.3 – 1.3</td>
<td>0.05 – 0.7</td>
<td>-20 – 30</td>
<td>0 – 1</td>
<td>30 – 6000</td>
<td>1 – 20</td>
<td>0.5 – 1.0</td>
<td>0 – 900</td>
</tr>
</tbody>
</table>

Table 1. Range of parameters used in the sensitivity study. For each range, six points were linearly spaced within the range. This amounts to $6^8$ (roughly $1.7 \times 10^9$) combinations of input variables to be evaluated.

The values in Table 1 were then used to construct the Jacobian (Eq. 4) for every combination of the input variables. The columns of interest for this work are those columns in the Jacobian containing the sensitivity information of $L$ and $u^*$ since these are further needed in CAR-FMI. In addition to $L$ and $u^*$, the Jacobian comprise sensitivity information for $Q_h$, $Q_e$, $Q^*$, and $\theta^*$.

In Fig. (1), the sensitivity of the inverse Obukhov length ($L^{-1}$) is shown for all combinations of the input parameters listed in Table 1. $L^{-1}$ describes the atmospheric stability. For neutral conditions $L^{-1} \approx 0$. When $L^{-1} << 0$ the atmosphere is unstable, and when $L^{-1} >> 0$ the atmosphere is stable. The figure serves as an illustrative example of the study. For clarity, Fig. (1) is further separated into a low wind speed situation with all other input variables varied (the main figure). The insert figure contains all combinations of input parameters associated with wind speeds in the range of $4 – 20$ m/s. The figure is separated into a low and high wind speed situation because the model is so much more sensitive at low wind speeds.

As can be seen from Fig. (1), $L^{-1}$ is most sensitive to a change in $U$. When compared to the insert ($4 \leq U \leq 20$ m/s), the sensitivity to a change in wind speed is more pronounced at low wind speeds. First, let us consider the situation when $L^{-1}$ is negative at low wind speeds. When $L^{-1}$ is negative, which is the case for unstable and neutral conditions, the derivative $\partial L^{-1}/\partial U$ is positive. That means that an increase in $U$, when $L^{-1} < 0$, will always tend to favour the estimate of the stability to become more neutral. That is, a negative $L^{-1}$ and a positive derivative $\partial L^{-1}/\partial U$ will therefore move $L^{-1}$ towards neutral should $U$ increase.

On the opposite, when $L^{-1} > 0$ (i.e. stable or neutral), then $\partial L^{-1}/\partial U$ is always negative. That implies that a increase in $U$ will therefore, again, tend to make $L^{-1}$ move towards neutral. This is in agreement with what
one would expect in nature since an increase in $U$ will induce mechanical turbulence regardless of the initial stability and hence favour neutral conditions. At higher values of $U$, seen in the insert of Fig (1), the $L^{-1}$ range in now restricted to roughly the range of $-0.03$ – $0.01$ (i.e. neutral).

The second most important input variable for the MPP-FMI with regard to $L^{-1}$ is $R_S$. Since the derivative $\partial L^{-1}/\partial R_S$ of in all combination of inputs considered is always negative, and even more so when $L^{-1} > 0$, this implies that an increase in $R_S$ will always move the stability towards unstable. This follows the intuition that an increase in $R_S$ will increase turbulence due to buoyancy induced turbulence, and therefore favour unstable conditions. At low wind speeds, it has to be noted, that the spread in the sensitivity of $L^{-1}$ to $R_S$, is an indication that other meteorological input variables influence the results, especially when $L^{-1} > 0$. This is evident from the fact that the sensitivity to $R_S$ does not follow a single line, but is spread out. For example when $L^{-1} = 0.3$, then $\partial L^{-1}/\partial R_S$ is in the range of $-0.1$ – $0.6$. The highest sensitivity to a change in $R_S$, at low wind speeds, is when $R_S$ is close to zero and the surface albedo ($r$) is low. This information is, however, not colour coded into the figure not to degenerate the clarity of the figure.

ACKNOWLEDGEMENTS

This work was supported by Academy of Finland Center of Excellence program (project number 272041). John Backman wishes to acknowledge Maj and Tor Nessling foundation grant 2014044 and 201600449 for financial support.
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INTRODUCTION

Atmospheric new particle formation (NPF) events, i.e. nucleation and subsequent growth of the newly formed particles have received increasing attention due to their impact on climate and human health (Kulmala et al., 2004; Minguillón et al., 2015 and references therein). Despite many studies and findings about NPF events, several features at the nucleation level including the actual mechanism, vapors involved, and the actual formation rate are still remained unknown (Kulmala et al., 2006; Lehtinen et al., 2007). This is partly because the cut-off size of the instruments, which measure the particle size distributions, do not extend to nucleation size range but typically are 3 nm or even larger (e.g. 7 or 10 nm). This limits the use of the particle data in NPF studies and challenges understanding the NPF globally. In this study, we report estimations of 3 nm particle formation rates $J_3$ for the Puijo (Finland) site where size distribution measurements have been only down to 7 nm in diameter. Thus, we use a scaling method based on aerosol dynamics theory for the range 3 - 7 nm. However, we first validate our method to estimate $J_3$ using the data at Hyytiälä where particle number size distribution measurements extend down to 3 nm. In this study, we use the method presented in Lehtinen et al. (2007) in which particle growth rate is assumed to be time and size independent. The coagulation sink is also assumed time independent and self-coagulation within nucleation mode is considered negligible.

METHODS

In this study we used the aerosol number size distribution measurements from two different stations in Finland: SMEAR II located in Hyytiälä and SMEAR IV in Kuopio. SMEAR II (Hyytiälä, southern Finland; 61°51’N, 24°17’E, 181 m a.s.l.) is characterized by boreal coniferous forest. The aerosol number size distributions at SMEAR II are measured with a Differential Mobility Particle Sizer (DMPS; Aalto et al., 2001) with a cut-off size at 3 nm. We analyzed the data between years 2000-2012. At SMEAR IV the instruments are set up at the top of Puijo observation tower (62°54’32”N, 27°39’31”E, 306 m a.s.l., and 224 m above the surrounding lake level). The aerosol size distribution is measured with a twin-DMPS covering the size range 7-800 nm (Leskinen et al., 2009). In this study we analyzed aerosol size distributions measured between April 2007 and December 2015.
An analytical formula is presented in Lehtinen et al. (2007) which links the “real” particle formation rate and the “apparent” formation rates of particles of larger sizes (typically above 3 nm). This formula was first derived by Kerminen and Kulmala (2002) and was later modified by Lehtinen et al. (2007). To evaluate the formula for atmospheric data, we used the data on evolution of particle size distribution during NPF event days from SMEAR II. We used the equation in Lehtinen et al. (2007) to calculate apparent formation rate at 3 nm ($J_{3, \text{est}}$) from measurements as follows:

$$J_{3, \text{est}}(t) = J_{7, \text{obs}}(t') \cdot \exp\left(\gamma(t).d_1 \cdot \frac{CoagS(d_1=3\text{nm})}{GR_{3-10}}\right),$$

with \(\gamma = \frac{1}{m+1} \left(\left(\frac{d_x}{d_1}\right)^{m+1} - 1\right)\) and \(m = \frac{\log[CoagS(d_2)/CoagS(d_1)]}{\log[d_x/d_1]}\),

Where $J_{7, \text{obs}}$ indicates the observed formation rate of 7-nm particles. $CoagS$ is coagulation sink of particles in nucleation mode onto the background particles, and $GR$ is the particle growth rate which is assumed to be time and diameter independent. Note that we set $d_1 = 3$ nm and $d_x = 7$ nm.

We used a similar approach to Kulmala et al. (2012) and Vuollekoski et al. (2012) to calculate the observed apparent formation rate of particles of 3 nm ($J_{3, \text{obs}}$) and 7 nm ($J_{7, \text{obs}}$) in diameter from measured aerosol size distribution:

$$J_{3, \text{obs}} = \frac{dN_{3-7}}{dt} + \frac{dN_{9-5}}{9-5} \cdot GR_{7-20} + N_{3-7} \cdot CoagS(d_{\text{GMD}})$$

(2)

where the geometric mean diameter of investigated size range was $d_{\text{GMD}} = \sqrt[3]{7}$ nm.

$$J_{7, \text{obs}} = \frac{dN_{7-10}}{dt} + \frac{dN_{12-8}}{12-8} \cdot GR_{7-20} + N_{7-10} \cdot CoagS(d_{\text{GMD}})$$

(3)

where $d_{\text{GMD}} = \sqrt[7]{10}$ nm.

Here $N_{3-7}$, $N_{5-9}$, $N_{9-5}$, $N_{12-8}$ and $N_{7-10}$ are the number concentration of particles within size ranges 3-7 nm, 5-9 nm, 7-10 nm and 8-12 nm, respectively. Note that the terms $\frac{dN_{9-5}}{9-5}$ and $\frac{dN_{12-8}}{12-8}$ present the size distribution function at 3 nm and 7 nm, respectively. The coagulation sink ($CoagS$) terms were calculated directly from the measured particle size distributions and the hygroscopicity effects was taken into account using the parametrization of Laakso et al. (2004). There is a time-lag (due to growth of particles from 3 nm to 7 nm) between $J_{3, \text{est}}$ at time $t$ and $J_{7, \text{obs}}$ at time $t'$ which is calculated using $t = t' - \frac{t_{\text{nm}}}{GR_{3-10}}$. In addition, the $m$ and $CoagS(d_1)$ values in eq. (1) are calculated as medians of the corresponding values during time $t$ to $t'$. To determine the growth rates required in this study, we used the automated algorithm developed by Hussein et al. (2005) which fits log-normal modes to the measured aerosol size distributions. The algorithm assumes that the size distribution is a superposition of 1-3 log-normal modes and at each measurement time optimizes the geometric mean diameter, total number concentration and standard deviation of each mode to fit the measurements. The $GR$ is calculated from time development of the geometric mean diameter of nucleation mode.

Figure 1 shows the estimated formation rates $J_{3, \text{est}}$ (eq. 1) against the observed ones $J_{3, \text{obs}}$ (eq. 2) in Hyytiälä. We analyzed 66 clear NPF event days for which the formation and growth rates could be determined. Each data point in Figure 1-a indicates the arithmetic mean of the $J_{3, \text{est}}$ and $J_{3, \text{obs}}$ for a single NPF day during the time window from 07:00 to 19:00 local time. The results show that the $J_{3, \text{est}}$ mean values agree reasonably well with $J_{3, \text{obs}}$ with correlation coefficient 0.78 and 85 % of $J_{3, \text{est}}$ values are within the factor of two of the $J_{3, \text{obs}}$ values. Equation 1 seems to slightly overestimate the formation rate of 3-nm particles. The arithmetic
mean of all $J_{3,obs}$ and $J_{3,est}$ data points (the total mean) are 0.23, 0.27 # cm$^{-3}$ s$^{-1}$, respectively. The total means of $J_{3,obs}, J_{3,est}$ were 0.24, 0.31 # cm$^{-3}$ s$^{-1}$ after replacing $GR_{3-10}$ with $GR_{7-20}$ that will be needed when estimating $J_{3,est}$ values in Puijo. The results obtained from validation of Hyytiälä data show that eq. (1) estimates the mean formation rates of 3-nm particles with reasonably good agreement with observations. However, detailed time-evolution of the 3-nm particle formation rates are poorly predicted using eq. (1) due to unsatisfactory $GR$ estimates.

At Puijo, we calculated the $J_{3,est}$ mean values for 73 clear NPF events. The mean and median of $J_{7,obs}$ for quantifiable NPF days were 0.24 and 0.11 cm$^{-3}$ s$^{-1}$, respectively, while the estimated mean and median $J_{3,est}$ were 0.45 and 0.19 cm$^{-3}$ s$^{-1}$, respectively.

![Figure 1. Estimated $J_{3,est}$ against observed $J_{3,obs}$ formation rates of 3-nm particles (#cm$^{-3}$ s$^{-1}$) during NPF event days in Hyytiälä. Data points indicate arithmetic mean $J_{3}$ during 07:00 to 19:00 local time for each NPF day.](image)

ACKNOWLEDGEMENTS

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REFERENCES


UNDERSTORY MEASUREMENTS OF BIOGENIC VOLATILE ORGANIC COMPOUNDS BY SOLID-PHASE MICROEXTRACTION AND PORTABLE GAS CHROMATOGRAPHY-MASS SPECTROMETRY


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Keywords: BVOCS, SOIL CHAMBERS, SPME, PORTABLE GC-MS.

INTRODUCTION

Terrestrial vegetation introduces to the atmosphere an enormous diversity of biogenic volatile organic compounds (BVOCs), which consist of a large variety of molecules that differ in size, physicochemical properties and metabolic origin (Peñuelas and Staudt, 2010). Many of these compounds are extremely lipophilic and have enough vapour pressure to be released into the atmosphere in significant amounts (Loreto et al., 2010). Some BVOCs, such as monoterpenes, are oxidized in the atmosphere and the oxidation products formed can participate in the formation of secondary aerosol particles (SOA) (e.g. Riipinen et al., 2012). Other organic volatiles, including aldehydes, can participate in atmospheric photolytic reactions and contribute to new particle formation (Hellén et al., 2004). Aerosols have a significant impact on climate, both directly by scattering and absorbing radiation, and indirectly by acting as a cloud condensation nuclei (CCN) that affects cloud properties (Zelenyuk et al., 2010). BVOC fluxes from the boreal forest canopies have been intensively studied but forest floor and understory emissions can also contribute significantly to the boreal forest ecosystem (Aaltonen et al., 2013). In this research, solid-phase microextraction (SPME) combined with portable gas chromatography-mass spectrometry (GC-MS) was used for the in-situ measurement of BVOCs from soil chambers, and for characterization of the most abundant species emitted from understory vegetation. Ambient samples were simultaneously collected and measured for comparison purposes. Results were also compared with PTR-MS measurements of monoterpene fluxes.

METHODS

BVOC measurements from soil chambers were performed in summer 2015 at the Station for Measuring Ecosystem-Atmosphere Relations, SMEAR II in Hyytiälä, Finland. The first part of the campaign occurred from 23rd to 28th of June for testing and optimization of the method used, including fiber exposition time inside the chambers, repeatability, ambient air sampling time and validation of the method with conventional GC-MS. The second part of the campaign occurred from 5th to 27th of August for the sampling and analysis of BVOCs from soil chambers and ambient air by SPME and portable GC-MS. Sampling was performed by using CUSTODION® solid phase microextraction syringes (DVB/PDMS, 65μm film thickness). The method consisted of a closure of the chambers during 5 minutes, insertion of the SPME fibers inside the soil chambers, and collection for 40 minutes. Ambient samples were collected by using simultaneously two home-made SPME dynamic sampling system (flow rate of 11 L/min), installed at 30 cm height from the ground vegetation (Barreira et al., 2015). The dynamic sampling time...
was 60 minutes. A comparison between portable and conventional GC-MS analysis was performed by inserting two SPME fibers inside the chambers after a closure time of 5 min, simultaneous collection of the samples during 40 minutes, and analysis of the samples by both instruments. On-field analysis was performed by a portable gas chromatograph-mass spectrometer (GC-MS) that consisted of a low thermal mass injector, a low thermal mass capillary gas chromatograph and a miniature toroidal ion trap mass spectrometer (an example of a chromatogram is represented in Fig. 1).

CONCLUSIONS

Air samples were collected simultaneously from soil chambers and ambient air by static and dynamic SPME, respectively, to compare the type and relative amounts of VOCs found in soil samples with those found in ambient air. Sample preparation was avoided, resulting in reduced analysis time, sample contamination and potential losses during analytical process. The most abundant BVOCs measured in chambers and ambient air were α-pinene and Δ3-carene (Fig. 2). Other aldehydes with a recognized role on atmosphere physics and chemistry were also measured (Fig. 3). A concordance between amounts of monoterpenes measured from soil chambers by portable GC-MS and monoterpene fluxes measured by PTR-MS was observed. The contribution of each BVOC compounds to understory concentrations was estimated. Ambient amounts were significantly higher when wind direction was from South-East, as a consequence of transportation of VOCs from the nearby sawmills. Results demonstrated the potential and versatility of the applied method for the rapid on field measurement and characterization of organic gaseous compounds. Although the study provided additional information about understory and ambient air composition, long-term measurements combined with laboratory studies from soil and plant emissions are still required to clarify the importance of studied compounds to the atmospheric processes.

Figure 1. Chromatogram obtained for a sample collected from a soil chamber by static SPME and analysed by portable GC-MS.
Figure 2. Amounts (peak area) of monoterpenes measured by portable GC-MS. Samples were statically collected from soil chambers and dynamically collected from ambient air. Monoterpene fluxes [ng·m⁻²·s⁻¹] measured from the soil chambers by PTR-MS were included for comparison.

Figure 3. Amounts (peak area) of aldehydes measured by portable GC-MS. Samples were statically collected from soil chambers and dynamically collected from ambient air.
ACKNOWLEDGEMENTS

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REFERENCES


NUCLEATION AT HIGH ALTITUDE: FROM THE ALPS TO THE EVEREST

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Keywords: NUCLEATION, FREE TROPOSPHERE, MASS SPECTROMETRY, IONS.

INTRODUCTION

A significant fraction (>50%) of cloud condensation nuclei (CCN) in the atmosphere arises from new-particle formation (Merikanto et al., 2009; Yu and Hallar, 2014) where 35% are directly formed in the free troposphere (Merikanto et al., 2009). While particle nucleation has been observed almost everywhere in the atmosphere (Zhang et al., 2012), the mechanisms governing this process are still poorly understood and subject of on-going 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 from vapours in the free troposphere. For example, 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). Together with ubiquitous water vapour (H₂O), H₂SO₄ is believed to be the main source of new particles in the middle and upper troposphere (Lovejoy et al., 2004). However, no study has hitherto confirmed this hypothesis. So far, most nucleation measurements have been performed in the planetary boundary layer (Kulmala et al., 2013) or by airplane (Mirme et al., 2010). Within the relatively warm boundary layer, H₂SO₄ alone cannot explain either the particle formation rate or subsequent growth rate (Kirkby et al., 2011). 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 recent instrument developments, only a few studies have observed new-particle formation at high altitude (Garcia et al., 2014; Rose et al., 2015; Venzac et al., 2008) and even fewer have managed to measure down to 1 nm in size using the Neutral cluster Air Ion Spectrometer (NAIS). These
measurements have shown that new-particle formation can take place with high frequency at high altitudes. However, none of these previous studies at high altitude have measured the chemical composition of the growing clusters. Therefore, while these studies confirm that new-particle formation at high altitude is important, they are insufficient to allow for a reasonable evaluation of the mechanisms in order to improve the accuracy of new-particle formation representation in models. A detailed framework that unifies the particles’ physical properties and the vapours’ chemical composition is required to understand from first principles the fundamental pathways by which 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**

In order to monitor and characterize new particle formation processes, measurements were performed first at the Jungfraujoch high alpine site in Switzerland as part of the NUcleation Cloud and Aerosol Characterization Experiment (NUCLACE), which took place from January 2013 to March 2014. The measurements were conducted in the Sphinx laboratory (3580 meters asl), which is situated between the Mönch (4099 meters asl) and the Jungfrau (4158 meters asl). More information on this site and on the long-term aerosol measurements performed at Jungfraujoch can be found elsewhere (Bianchi et al., 2016; Tröstl et al., 2016b). The second set of measurements was conducted at the Himalayan Nepal Climate Observatory Pyramid (NCO-P) situated on the southern slope of the Himalayas, not far from the Everest base camp (5079 meters asl). Pictures of the measurement sites are shown in Figure 1 and the set of instruments used in these campaigns are listed in Table 1.

<table>
<thead>
<tr>
<th>Device</th>
<th>Measured property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric Pressure interface Time-Of-Light mass spectrometers (APi-TOF)</td>
<td>Chemical composition of the positive and negative ions ($D &lt; 2$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 ($D &lt; 2$nm)</td>
</tr>
<tr>
<td>Neutral and Air Ion Spectrometer (NAIS)</td>
<td>Particle and ion size distribution from $D = 0.4$ to 40 nm</td>
</tr>
<tr>
<td>Nano Scanning Mobility Particle Sizer (Nano-SMPS)</td>
<td>Particle size distribution from $D = 4$ to 100 nm</td>
</tr>
<tr>
<td>Condensation Particle Counter (CPC)</td>
<td>Particles number concentration ($D &gt; 2.5$ nm)</td>
</tr>
<tr>
<td>Particle Size Magnifier (PSM)</td>
<td>Particle number concentration ($D &gt; 1$ nm) and growth rate between $D = 1$ and 2.3 nm</td>
</tr>
</tbody>
</table>

Table 1. Instruments used at the Jungfraujoch high alpine site in Switzerland and at the Himalayan Nepal Climate Observatory Pyramid (NCO-P).

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 nm and a PSM were used. PSM measures particles with a cut off that varied from 1-4 nm (charged ammonium sulphate equivalent diameter). Besides this set of instruments specific for the observation of nucleation events other parameters like ozone and sulphur dioxide concentration are measured by the Swiss National Air Pollution Monitoring Network (NABEL) and by the NCO-P station.
CONCLUSIONS

Many nucleation events have been observed and characterized at the Jungfraujoch as well as the Pyramid station in Nepal. Most of the observed nucleation events occurred during clear sky conditions, however the physics of the two locations was quite different being Jungfraujoch in top of a mountain and the pyramid station in the bottom of the valley.

With the study conducted at the Jungfraujoch we provide observational evidence that at high altitudes, new particle formation occurs mainly through condensation of HOMs, in addition to taking place through sulfuric acid–ammonia nucleation. Neutral nucleation is more than 10 times faster than ion-induced nucleation, and growth rates are size-dependent. New-particle formation is restricted to a time window of 1 to 2 days after contact of the air masses with the planetary boundary layer; this is related to the time needed for oxidation of organic compounds to form HOMs. More details on this study can be found in Bianchi et al., (2016).

The Nepal measurements took place one year after and therefore the data analysis is still on progress. For the first time, an instrument like the APi-TOF has been deployed at high altitude (i.e. 5079 meters asl). Figure 2 shows the first APi-TOF mass spectrum running in negative mode recorded above 5000 m asl during a new-particle formation event. The main ions that have been identified so far are all deprotonated acids: sulfuric acid, nitric acid, malonic acid, methanesulfonic acid and iodic acid. It is worth noting that larger ions are formed by different combinations of identified acids (i.e. $H_2SO_4HSO_4^-$, $CH_3SO_2H^+HSO_4^-$, etc.).
Figure 2. Mass spectrum of negative ions recorded during a new-particle formation event at NCO-P, Nepal, 5079 m asl.

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REFERENCES

INTRODUCTION

Within the framework of the implementation of the project of joint Russian-European Studies were carried out research on dynamics of natural and anthropogenic emissions of trace gases and aerosols over the Russian Federation in the period 2010-2015 with use of remote sensing data. Developed during the project methods and tools to monitor the dynamics of emissions of trace gases and aerosols based on satellite data remote sensing data (TERRA, AQUA, AURA and Suomi NPP satellites) provide data for comprehensive monitoring of air pollution.

METHODS

Satellite monitoring is based on spatial-temporal analysis and long-term variability of the quantities of atmospheric emissions of pollutants (CO2, NO2, SO2, aerosols etc.) from wildfires, and climate-relevant anthropogenic sources in the Russian Federation with the use of remote sensing data (Bondur, 2011, Bondur, 2011a, Bondur, 2014).

Based on the method of calculating the volume of emissions from wildfires (Seiler, Crutzen, 1980) the MODIS (TERRA / AQUA satellites) data series have been analysed for the European part of Russia. Figures 1 and 2 presents the distribution of the wildfires areas and corresponding aerosol emissions in the European part of Russia from April to October 2010-2015.

Figure 1. Histogram of wildfires area distribution in the European part of Russia from April to October of 2010-2015.
Analysis of the experimental results showed that the majority of natural fires in the European part of Russia falls on the April and the hottest summer months of July and August (Bondur, 2015, Bondur, Ginsburg, 2016). The maximum area covered by the wildfire for the region were recorded in August 2010. The graphs of emissions volume practically repeat the wildfires area distribution. However, the area wildfires in the European part of Russia in July 2010 has been significantly reduced in comparison with July 2011, while the volume of CO emissions, CO2 is much greater (Bondur, 2015; Bondur, Ginsburg, 2016).

The dynamics of the emissions from anthropogenic sources has been analysed on the base of NO2 and SO2 data series obtained from OMI instrument (AURA satellite) in the period from 2012 to 2015 over the European part of Russia. OMI data have been processed with spatial smoothing algorithm presented in Fioletov et al., 2011. For NO2 were built weekly, monthly and seasonal concentrations distribution maps, and for SO2 were considered only seasonal fluctuations in summer (see. Fig. 3 and 4).

Figure 2. Histogram of PM 2.5 emission volumes in the European part of Russia from April to October of 2010-2015.

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Figure 3. Mean monthly NO2 over European Russia for summer period 2014 measured by OMI

Figure 4. Mean summer season SO2 over European Russia for 2012-2015 measured by OMI
The statistical analysis of SO2 variation showed that the average background value of SO2 over the European part of Russia is 0.01 Dobson. Areas characterized by higher than background concentrations of SO2 were analyzed with the use of Wikimapia data to identify the potential sources of emissions. Based on the repeated average seasonal fluctuations of SO2 concentrations measured by OMI 45 industrial sources of SO2 have been detected.

VIIRS Night Fire thermal data (SC Suomi NPP) (Elvidge C. et al, 2013) were used to identify groups of anthropogenic and natural sources of trace gases emissions with further assessment of the CO2 emissions equivalent dynamics over the Russian Federation in the period 2014-2016. On the of temperature variations obtained from satellite data, it was built a map of the spatial distribution of different types of emission sources over the Russian Federation (see. Figure 1.5).

Finally, the heat sources were divided into four main groups based on spatial clustering and the average temperature of the source, as well as the frequency coverage during the year.

As a result of the spatial-temporal analysis of the data was developed a geodatabase with statistical information on 111 sources— gas flares, powerful enough to detect them from space. CO2 emissions equivalent was calculated for 2 years period allowing to evaluate the trends of growth or fall of emissions for each object (Fig. 6).

According to the case study of gas flares as emission sources detected on VIIRS Night Fire data, 33% of the objects tend to increase emissions, 47% - to a reduction in emissions, and 20% are characterized by a constant volume of emissions during the period from March 2014 to February 2016.
CONCLUSIONS

The result of current research confirmed the ability to identify sources of natural emissions from wildfire on multispectral satellite data of the MODIS (TERRA / AQUA) with a temporal resolution of 4 hours, and also to calculate the volume of trace gases and aerosols emissions (including CO CO2, NO2, etc.) on the base of remote sensing data at different spatial levels. Long-term series of seasonal OMI data (AURA) can be successfully used to identify the major sources of industrial emissions of sulphur compounds, as well as to monitor the dynamics of SO2 emissions from identified sources. Spatio-temporal analysis of the VIIRS Night Fire Data Set (Suomi NPP) for the test area showed that anthropogenic sources such as large gas flares and industrial sites can be correctly identified with a probability of more than 80% on satellite data. For the careful assessment of gas flares emission it is required statistical processing of long-term data series, as soon as simultaneous shooting can cause extreme values, significantly distorting the average characteristics of the gas burning.

ACKNOWLEDGEMENTS

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HYGROSCOPICITY OF SUB 30NM PARTICLES DURING CLOUD 10

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Keywords: HYGROSCOPICITY, HTDMA, SECONDARY ORGANIC AEROSOL, CLOUD.

INTRODUCTION

The impact of aerosol particles on the atmosphere and climate depends strongly on their ability to take up water vapour (hygroscopicity) and act as cloud condensation nuclei. The hygroscopicity of particles is determined by the composition and the size of the particles. Sulfuric acid (H$_2$SO$_4$), ammonia and oxidized organic vapours play an important role in new particle formation of secondary organic aerosol (SOA) and growth of those particles. In general, H$_2$SO$_4$ and its salts have much higher hygroscopicity than organic compounds found in SOA particles. Thus, size resolved hygroscopicity measurements may give valuable insights into the composition of these small particles as direct measurements of the chemical composition of sub 30 nm particles are quite challenging. In this study, we investigated the impact of a range of different factors (e.g. organic precursors, oxidation conditions) on hygroscopicity and thus on composition of sub 30 nm particles.

METHODS

The CLOUD chamber at CERN was designed to study new particle formation and the early stages of particle growth. Details on the setup and characterisation can be found in Kirkby et al. (2011). During the CLOUD10 campaign a range of different conditions (e.g. organic precursors, oxidation conditions) was studied aiming at mimicking atmospheric relevant processes as best as possible. In Table 1 the range of conditions in the CLOUD chamber during this study is summarised. α-pinene and Δ-3-carene are monoterpenes which are typical for emissions in boreal forests.

<table>
<thead>
<tr>
<th>condition</th>
<th>range</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic precursors</td>
<td>α-pinene</td>
</tr>
<tr>
<td></td>
<td>Δ-3-carene</td>
</tr>
<tr>
<td></td>
<td>α-pinene + Δ-3-carene</td>
</tr>
<tr>
<td>[organic precursor]</td>
<td>100 – 1500 ppt</td>
</tr>
<tr>
<td>[H$_2$SO$_4$]</td>
<td>$10^4$ – $5 \times 10^7$ /cm$^3$</td>
</tr>
<tr>
<td>[NO$_x$]</td>
<td>0 – 15 ppb</td>
</tr>
<tr>
<td>[O$_3$]</td>
<td>40 ppb</td>
</tr>
<tr>
<td>temperature</td>
<td>-25 ºC, +5 ºC, +25 ºC</td>
</tr>
<tr>
<td>RH</td>
<td>40 %</td>
</tr>
</tbody>
</table>

Table 1. Range of experimental conditions

The hygroscopic growth factor at 90% RH was measured with a custom built Hygroscopicity Tandem Differential Mobility Analyser (nanoHTDMA) for particles of sizes from 10 to 25 nm (Keskinen, 2011).
Then the hygroscopicity parameter $\kappa$ was calculated based on the method by Petters and Kreidenweis (2007).

As the $\kappa$ values for pure $\text{H}_2\text{SO}_4$ and $\alpha$-pinene derived SOA are known, the volume fractions of organics and $\text{H}_2\text{SO}_4$ in the particles can be calculated with the simple Zdanovskii–Stokes–Robinson (ZSR) mixing rule. A $\kappa$ of 0.7 was used for $\text{H}_2\text{SO}_4$ and for $\kappa_{\text{org}}$ the lowest average value measured here was used ($\kappa_{\text{org}}=0.08$).

RESULTS AND CONCLUSIONS

In this study, the hygroscopicity $\kappa$ of 10 - 25 nm particles is mostly determined by gas phase $[\text{H}_2\text{SO}_4]$ and organic precursor concentration with higher $[\text{H}_2\text{SO}_4]$ leading to a higher fraction of $\text{H}_2\text{SO}_4$ in the particles and thus higher $\kappa$ (see Fig 1). $\kappa$ values decreased with increasing organic precursor concentrations while the type of organic precursor did not alter them. However, the investigated precursors are very similar (monoterpenes) and a broader range of compounds may lead to different findings. Organic volume fractions of 0.6 to 1.0 were found when the $\kappa$ was converted with the ZSR approach. Only very small differences were found between the hygroscopicity of 10 nm and 25 nm particles with slightly higher $\kappa$ for smaller particles. This suggest, that already at these sizes the organic fraction dominates the particle phase and the ratio of organic compounds and $\text{H}_2\text{SO}_4$ in the particles is determined by the gas phase conditions. The influence of the particle size is negligible in this range.

![Figure 1. $\kappa$ vs gas phase $[\text{H}_2\text{SO}_4]$ and organic precursor concentration (colour code). $\kappa$ increases with increasing gas phase $[\text{H}_2\text{SO}_4]$ and decreasing organic precursor concentration](image)

Gas phase $[\text{NO}_x]$ did not influence the observed $\kappa$ in the investigated range. But no particles grew above the detection threshold of the nanoHTDMA (>10nm) when $[\text{NO}_x]$ was higher than 8 ppb. This limitation in particle formation/growth is most likely due to the coupled system in the chamber where $\text{NO}_x$, HO, O$_3$ and $\text{H}_2\text{SO}_4$ chemistry are closely linked and this cannot be directly extrapolated to other conditions (e.g. ambient).
No straight forward link between $\kappa$ and CLOUD temperature was found. But any such effect (e.g., partitioning of more volatile compounds into the particle phase at lower temperatures) may be cancelled by the fact that the particles were warmed to room temperature before measurements in the nanoHTDMA.

ACKNOWLEDGEMENTS

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AIR IONS IN THE NORTHERN AMAZON: INSIDE VS. OUTSIDE CANOPY CONDITIONS

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Keywords: AMAZON, IONS, RAIN EVENTS, NEW PARTICLE FORMATION.

INTRODUCTION

New particle formation (NPF) has been observed under an array of environments across the world (Kulmala et al. 2004; Manninen et al. 2010), both over land and ocean, and across altitudes from ground level to the free troposphere. And while the fraction of primary (directly emitted) versus secondary particles (formed in the atmosphere) can vary across locations (Kulmala et al. 2016), NPF has been shown to contribute significantly to the total atmospheric particle loading, and an accurate quantification of this process at a global scale is needed for better climate model predictions (Jokinen et al. 2015). However, NPF events have been elusive in the Amazon Basin, despite numerous measurement campaigns since the mid 1980’s (Martin et al. 2010). Nucleation mode particles that have been observed occur at large sizes, indicating NPF likely began at cloud outflow in the free troposphere and was transported to ground level via downdrafts (Zhou et al. 2002). This study contributes to identifying the concentrations and characteristics of ions and neutral particles in the nucleation mode within the northern Amazon Basin, as part of the GOAmazon 014/15 campaign. Our data includes long-term inside canopy measurements from December 2011 to January 2014 (ZF2 site), and continues with two intensive observational periods (IOPs) at a clearing site (T3) during the dry and wet season, respectively. Specifically, we identify rain events inside the rainforest canopy, possibly as a result of ion generation due to the balloelectric effect; and for the first time to our knowledge, we present NPF events occurring at ground level of the Amazon Basin in the T3 clearing site.

METHODS

The dataset analysed in this study compares ions and particles concentrations inside rainforest canopy with those in a clearing site within the Amazon Basin. Site ZF2 covers long-term measurements from December 2011 to January 2014 inside a 30-m rainforest canopy, some 60 km north of Manaus, Brasil (–2.609S, –60.2092W; REF). An ion spectrometer (NAIS, Manninen et al. 2016) was placed 2 m above ground, with a detection range of 0.8-40 nm ions of both polarities. Site T3 is located in a clearing near Manacapuru, 70 km downwind of Manaus (–3.2133°S –60.5987°W) as part of the ARM Mobile Facility where two IOPs were conducted from Feb–Mar 2014 for the wet season, and Sep–Oct for the dry season. The same NAIS instrument was transported from Site ZF2 to T3 for ion measurements. Additionally, Site T3 included an ultrafine condensation particle counter (uCPC) and a particle size magnifier (PSM) to detect sub-3 nm aerosol particles.
RESULTS AND CONCLUSIONS

A clear difference in ion diurnal concentrations between sites is the evidence of boundary layer development during the early morning hours that is clearly seen in the clearing Site T3, but is absent from Site ZF2, where the canopy is likely balancing ion sources and sinks and hindering the deep convection experiences at the clearing. Additionally, two types of events where particular to each site, namely rain-events inside the canopy site ZF2, and NPF events observed only in Site T3. This abstract focuses on Site ZF2.

Site ZF2- inside rainforest canopy. From December 2011 to January 2014, ion data for Site ZF3 resulted in 359 (45%) and 319 (37%) days presenting rain events in the negative and positive polarity, respectively; that is, an increase in nucleation mode ion concentration with the onset of rain. Conversely, 24% negative and 32% positive polarity data showed no ion concentration enhancement at any point in the 24 hours of the day. During rain-events a correlation of ion concentration with rain intensity (Fig. 1) hints at a breakdown of charged rainwater droplets as the likely source for the ion concentration enhancement. Elevated ion concentrations $>10^3$ can be seen in Figure 1, and are likely due to the electrometer of the NAIS instrument saturating during highest relative humidity (RH; as the colorbar), and not represent actual ambient ion concentrations. Further analysis is undergoing to differentiate between the rain-induced ions and their decay rate, and instrumental noise. In addition to rainwater ions, future work includes investigating the effect of thunderstorm in ion production at both sites.

ACKNOWLEDGEMENTS

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LINKING STEM GROWTH RESPIRATION TO THE SEASONAL COURSE OF STEM GROWTH AND GPP OF SCOTS PINE

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Keywords: GROWTH, RESPIRATION, DENDROMETERS, RADIAL VARIATIONS, GPP, GROWTH EFFICIENCY, EDDY COVARIANCE.

INTRODUCTION

The physiological costs to maintain and grow woody tissue, and its contribution to net primary production (NPP) have been of great interest to researchers because of their contribution to tree and forest carbon budgets. This is especially true with NPP and its components: gross primary production (GPP) and respiration. These have been studied comprehensively in relation to carbon budgeting and biomass growth (Ryan, Lavigne et al. 1997, Xiao, Yuste et al. 2003, Goulden, McMillan et al. 2011). On the ecosystem level, studies have examined respiration using eddy covariance measurements, which can estimate respiration and GPP with high accuracy (Desai, Richardson et al. 2008). However, understanding individual tree organ’s contribution to ecosystem respiration is still unclear (Waring, Landsberg et al. 1998). This concern is further exacerbated when studies have used different methodologies to measure growth and respiration. For example, previous studies have used dendrometers to quantify appreciable stem increment over the growing season – a proxy for stem growth. However, it is now understood that these changes include water-related changes (Daudet, Améglio et al. 2005, Mencuccini, Hölttä et al. 2013, Chan, Hölttä et al. 2016, Zweifel 2016). Although these changes are small on a seasonal scale, on a daily scale, they can mask cambial growth. To overcome this problem, some studies have used dendrometers on a bi-weekly (Maier 2001), monthly (Vose and Ryan 2002, Zha, KELLOMÄKI et al. 2004) and annual (Araki, Kajimoto et al. 2014) scale. The consequence is the loss of daily dynamics and the direct linkage to growth respiration. It is important, then, to analyse stem growth and stem respiration on a daily scale to greatly understand these individual dynamics (and their linkage) over the growing season.

In this paper, the relationship between growth respiration \((R_g)\) and stem growth respiration is examined on a daily time scale of *Pinus sylvestris* L. (Scots pine). This paves the way for a better physiological understanding of tree growth dynamics. We also include linkages to estimated growth efficiency (using biomass growth) and to eddy covariance measurements of GPP and evapotranspiration. Using dendrometers to measure stem growth, we use a previously published model (Chan, Hölttä et al. 2016) to remove water-related changes revealing a proxy for stem growth. Our aims are to: (1) compare stem growth rate to \(R_g\) from model-estimated growth and direct (raw) dendrometer measurements; (2) identify the time lag between stem growth rate and \(R_g\); and (3) calculate the annual woody-tissue respiration budget and compare it to eddy covariance data and model estimates.

RESULTS

On a daily scale, stem growth rate and \(R_g\) correlation lacked consistency within year and year-to-year when using raw data. However, this contrasted results using model-estimated growth, which showed comparable inter- and intra-annual dynamics. Similar to previous studies examining stem growth rate and \(R_g\) dynamics (e.g. Stockfors and Linder (1998), Vose and Ryan (2002)), using model-estimated growth revealed a low correlation during the spring, increasing greatly during the summer rapid-growth period,
and slightly decreasing when growth has slowed. A cross-correlation analysis revealed a consistent one-day time lag of stem growth rate preceding $R_g$. This result, was revealed using model-estimated growth, while direct stem measurements did not reveal any time lag. Although previous studies have found no time lag (e.g. (Maier 2001, Vose and Ryan 2002, Zha, KELLOMÄKI et al. 2004)), these results may be due to the studies using large intervals (e.g. monthly/bi-monthly) or averaging the growth rates. This could ultimately mask the lag between respiration and growth rate (Maier 2001).

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THEORETICAL UNDERSTANDING ON THE RELATIONSHIP BETWEEN IONISING RADIATION AND MEASURED AIR IONS

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Keywords: ionising radiation, ionising capacity, air ions, ion balance.

INTRODUCTION

Ionising radiation is known for producing air ions via ionisation in the atmosphere (Israël, 1970; Harrison, 2004). However, not until our recent study (Chen et al., 2016a) on the linkage between variations in ionising radiation and observed air ions came out in the journal Atmospheric Chemistry and Physics (ACP) as a discussion paper, there existed only a few work attempting to toggle this relationship (Laakso et al., 2004; Hirskikko et al., 2007). Ionising radiation ionises air molecules first to produce primary ions, which then undergo a series of rapid and complicated transformations in the atmosphere via physical and chemical processes and possibly end up as molecular ions, cluster ions or other charged or neutral species. As shown by Chen et al. (2016a), although connections between variations in the ionising radiation and measured cluster ion concentrations could be observed, cluster ion concentrations could show distinct features from variations in ionising radiation. Moreover, Tammet et al. (2006) found that the ion production rate based on measurable air ion concentration is about 5 cm$^3$s$^{-1}$, which on average is only half of the ionising capacity - the potential production rate of ion pairs derived from ionising radiation, as reported by Chen et al. (2016a). Furthermore, atmospheric scientists in the aerosol field often employ formation rates ($J$) to characterise new particle formation (NPF) events (Kulmala et al., 2012). However, whether the formation rate of ions is a comparable parameter to the ionising capacity remains unclear. It is therefore crucial to understand these discrepancies in order to elucidate the air ion formation process from ionising radiation in the lower atmosphere and reveal its potential role in new particle formation.

METHODS

In this work, we sourced the theoretical approach by conducting investigation into the balance between ionising capacity and air ion concentrations. First of all, the current form of the balance equation, as presented by Tammet et al. (2006), was examined and possible improvements were included in setting up the revised balance equation. Next, we carried out a term-by-term comparison between the updated balance equation and the equation widely used for formation rates calculation to understand their interrelationship. Thirdly, the improved theory was applied to ambient data to approximate the concentration of air ions below detection limits. These ambient data were collected from Hyytiälä SMEAR II station (Hari and Kulmala, 2005), including number size distributions of air ions measured by a Balanced Scanning Mobility Analyser (BSMA) and an Air Ion Spectrometer (AIS), atmospheric radon activity concentrations recorded by a radon monitor (Paatero et al., 1994; Chen et al., 2016b), total gamma radiation detected by a gamma detector (Laakso et al., 2004), as well as meteorological data from the station long-term mast measurement. Finally, sensitivity tests will be performed to facilitate the determination of the contribution from different dynamical processes.

CONCLUSIONS

Our term-by-term comparison between the updated balance equation and the equation for determining formation rates of ions indicates that the ionising capacity and formation rate of ions are not directly
comparable terms to each other, but rather there is a hierarchical relationship between them. Preliminary results obtained by using the balance equation form proposed by Tammet et al. (2006) under a steady-state condition showed that ionising radiation was capable of producing about 2400 cm$^{-3}$ ion pairs, among which only about one third was detectable by the BSMA in the size range of 0.8-8 nm in mobility diameter (Fig. 1). By further subtracting the charged fraction of ions bigger than 8 nm estimated using the approximation from Wiedensohler (1988) on the diffusion charging theory proposed by Gunn (1956), the amount of ions below the lower BSMA size detection limit was found to be about 1000 cm$^{-3}$. Similar results were also obtained based on the AIS measurement. This large number of ‘missing’ ions could be responsible for the discrepancy between the ion production rate calculated by Tammet et al. (2006) and the ionising capacity derived by Chen et al. (2016a) from ionising capacity. Additionally, it may also suggest that the current parameterisation of rate coefficients used in the balance equation to account for different dynamical processes are associated with larger uncertainties than expected. This highlights the necessity of the investigation into the sensitivity test of different processes on the ion balance, which may further assist fine-tuning of the theory. The core of the study is under finalisation and a manuscript is in preparation.

Figure 1. Ion concentration estimated from ionising capacity based on the ion balance equation proposed by Tammet et al. (2006). The amount of ions beyond the Balanced Scanning Mobility Analyser (BSMA) capability of detection is shown in red and the amount below the lower size detection limit of BSMA in yellow.

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LONG-TERM ANALYSIS OF CLEAR-SKY NEW PARTICLE FORMATION EVENTS AND NON-EVENTS IN HYYTIÄLÄ

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Keywords: BOREAL FOREST, GROWTH RATE, FORMATION RATE, ATMOSPHERIC PARTICLES.

INTRODUCTION

For a long time, atmospheric aerosols have shown their effect on the environment and on human health. Studying those, then, helps increase knowledge of air quality and global climate. Aerosols which are condensed phase particles (1nm - 100µm) suspended in a carrier gas originate either from primary or secondary sources. While primary sources include combustion, sea-spray and dust, the secondary aerosols are mainly formed through a gas-to-particle conversion mechanism (Kulmala \textit{et al.}, 2004). Our focus lies on secondary gas-to-particle conversion, specifically new particle formation (NPF) events. Such events are observed and studied in many areas globally (e.g. Kulmala \textit{et al.}, 2004 and references therein) and are found to contribute to more than 50% of atmospheric aerosols (Kulmala \textit{et al.} 2016). In order to have a complete picture of this phenomenon, we have to understand the gas precursors and their clustering mechanisms as well as the environmental conditions that favour or limit NPF events. The aim of this study is to combine 20 years of measurements in boreal forest environment at SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relations) (Hari and Kulmala, 2005) in Hyytiälä, Finland with accumulated knowledge and advanced analysis focusing only on clear-sky NPF events.

METHODS

First, we select clear-sky days from the data set based on the median cloudiness parameter (P) within the NPF time window (9:00 – 12:00 h). The cloudiness parameter is the ratio of measured global radiation to the theoretical maximum and has values between 0 and 1; a 0.3 value of P signifies complete cloud cover, while 0.7 is complete clear-sky. Using the data set from 1996-2015, the clear-sky NPF event days and non-event days are compared in terms of trace gas concentrations, meteorological parameters, precursor gas concentrations and condensation sinks (CS). The precursor vapours involved in NPF are sulfuric acid (SA) and oxidized organic compounds (OxOrg) which we retrieve via well-developed proxies brought about by Petäjä \textit{et al.} (2009) and Kontkanen \textit{et al.} (2016), respectively. Comparison between clear-sky events and non-events is further refined via the calculated formation rate of 1.5 nm and 3 nm particles, $J_{1.5,C}$ and $J_{3,C}$, respectively. While $J_{1.5,C}$ is calculated via heteromolecular nucleation of one SA and one OxOrg molecule (Paasonen \textit{et al.} 2010), the formation $J_{3,C}$ integrates the growth rate (GR) of particles from size of 1.5nm to 3 nm into the Kerminen–Kulmala equation (Kerminen and Kulmala, 2002).
RESULTS

Our results showed that a higher frequency of NPF occurs during clear-sky conditions (Figure 1). Increased radiation favours formation of OH radicals as well as other photochemical reactions increasing SA concentration, which is the basic component of newly formed particles.

![Fraction of days which are classified as NPF events, NPF non-events, and undefined days during different sky cloudiness conditions.](image)

During clear-sky conditions, while nucleation precursors (SA and OxOrg) displayed higher concentrations during event days, CS and other trace gases have higher concentrations during non-events. This proves the effect of CS on attenuating or even preventing NPF. Also, using SA and OxOrg proxies to calculate the formation rates of 1.5 and 3 nm particles serves well and gives apparent differences between clear-sky events and non-events. Similarly, many other meteorological parameters including temperature (T) and relative humidity (RH) affect NPF. Thus, by using CS and ambient temperature, we were able to find a threshold above which no clear-sky NPF events occurred. The threshold is described by an equation which is able to separate almost 98% of the NPF events and non-events during spring time.

CONCLUSIONS

In this study, we use 20 years of data collected in the SMEAR II station combined with previous knowledge in order to characterize variables affecting NPF events. Concentrating only on clear-sky conditions, we were able to get new ways to separate NPF events and non-events. In clear-sky conditions, the meteorological parameters, trace gases concentrations and other studied conditions appeared to be similar to those presented in the previous studies which did not consider separating clear-sky days. However, by using monthly variations, the differences became more visible. Using clear-sky conditions appears to bring us one step forward towards understanding NPF events and predicting their occurrences in Hyytiälä. Our study serves as basis for future detailed comparison with observations to formulate stronger conclusions.

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CCN ACTIVITY OF BLACK CARBON PARTICLES COATED WITH ORGANICS OF VARYING SOLUBILITY

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Keywords: HYGROSCOPICITY, BLACK CARBON, CCN.

INTRODUCTION

Atmospheric aerosol particles influence the climate by absorbing the incoming solar radiation and thus directly heating the atmosphere (direct effect) and by acting as cloud condensate nuclei (CCN) that form cloud droplets (indirect effect) (Boucher et al., 2013). During past decades, black carbon (BC) or soot particles have been shown to cause positive radiation forcing when released into atmosphere in large quantities. These particles are typically emitted from incomplete combustion of fossil fuels and biomass burning (Bond et al., 2013). While BC particles are typically insoluble in water and possess low hygroscopicity, other more hygroscopic material can condense on them and thus increase their CCN activity (Henson 2007). In this study, we investigated the CCN activity of BC particles coated with organic compounds and modelled the hygroscopic properties with a shell and core model (Kumar et. al, 2011).

METHODS

As proxy for BC we used Regal Black 400R (Cabot Corporation). The organic compounds used as coating material were chosen because of their range of solubility in water. They were glutaric acid (396 g/L), levoglucosan (780 g/L) and succinic acid (808 g/L). Coated BC particles were characterised with a single column CCN-counter (Droplet Measurements Technologies), a Scanning Mobility Particles Sizer (SMPS)-system (TSI Inc.) and an Aerosol Mass Spectrometer (AMS) (Aerodyne Research Inc.). The experimental setup can be seen in figure 1.

![Figure 1](image-url)
Mobility Particle Sizer (SMPS) (TSI Inc.) and an Aerosol Mass Spectrometer (AMS) (Aerodyne Research Inc.)

Theoretical values for CCN activity were calculated using core and shell model described below (Kumar et. al, (2011)):

\[
 s = \frac{4\sigma M_w}{\rho_w R T D_p} \left( \frac{e_i D^3_{dry} \kappa}{D^3_p - e_i D^3_{dry}} \right) - A_{FHH} \left( \frac{D_p - e_i^{1/3} D_{dry}}{2D_{H2O}} \right)^{-B_{FHH}} 
\]  

(1)

Where \( s = S - 1 \) is equilibrium supersaturation, \( \sigma \) is surface tension of water, \( M_w \) is molar mass of water, \( \rho_w \) is the density of water, \( R \) is the gas constant, \( T \) is the temperature, \( D_p \) is the diameter of the droplet, \( e_i \) is the volume fraction of the substance \( i \) as defined below in eq. (2), \( D_{dry} \) is diameter of the dry particle, \( \kappa \) is the hygroscopicity parameter and \( D_{H2O} \) is the diameter of absorbed water molecule. \( A_{FHH} \) and \( B_{FHH} \) are adsorption activation theory parameters.

The volume fraction of a substance \( i \) is defined as

\[
 e_i = \frac{m_i / \rho_i}{\sum_j (m_j / \rho_j)} 
\]  

(2)

Where \( m_i \) is mass and \( \rho_i \) is density of component \( i \).

RESULTS AND CONCLUSIONS

Figure 1 illustrates the change of critical supersaturation with change of dry particle size. Three different BC core sizes were used: 150 nm, 200 nm and 250 nm. Solid lines show theoretical values and points mark measured supersaturation values. For the dark blue dots, the diameter values have been calculated from AMS data. For the light blue dots, the diameter values are from SMPS measurements. Data from succinic acid measurements is still under analysis.

Figure 1. Critical supersaturation \( s \) vs. dry particle mobility diameter \( D_{dry} \). Solid black line shows theoretical values for BC, green line for coating compound and red line for different coating thicknesses starting from core size. Points mark measurement results. Theoretical values were calculated using equations (1) and (2).

Theoretical shell and core model presented here accurately predicts the hygroscopic behaviour of the coated BC particles. Results also clearly demonstrate that organic coating drastically lowers the needed supersaturation for CCN activation compared to uncoated BC particles.
ACKNOWLEDGEMENTS

This work was supported by The Academy of Finland (272041, 259005), CRAICC, European Research Council (ERC Starting Grant 335478), and University of Eastern Finland Doctoral Program in Environmental Physics, Health and Biology.

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WATER RELATIONS IN SILVER BIRCH DURING THE BIRCH SAP EXUDATION PERIOD

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Keywords: BIRCH SAP EXUDATION, EMBOLISM REFILLING, SAP PRESSURE, SILVER BIRCH, TRANSPIRATION.

INTRODUCTION

Silver birch (Betula pendula) sap is a natural resource that has been collected in Boreal countries for consumption. Nowadays its collection is commercialized and exported e.g. from Finland. Although the increasing interest in this product, the mechanism of sap pressurization and its environmental drivers are not well understood. Traditionally, it is known that there is a sap exudation period at thawing when it is possible to collect it. During this period the xylem sap is under positive pressure and it finishes when buds burst and transpiration through the leaves starts inducing a release in the xylem pressure. During winter birch xylem water transport system has accumulated air due to freeze-thaw cycles and the consequent formation of winter embolisms (Sperry et al. 1994). At spring, during the sap-exudation period these embolisms are refilled with water. In this way the xylem water transport system gets recovered, and starts to work effectively. Our aim in this study is to quantify which environmental factors and physiological processes are involved in sap-flow and xylem pressure dynamic in birch under boreal spring conditions.

MATERIALS AND METHODS

We carried out our experimental measurements at SMEAR II measurement station in Hyytiälä, Southern Finland, during two years at spring time (2015 and 2016), and at a birch forest in Tohmajärvi, Eastern Finland (during 2014 and 2015). As birch water relations variables we measured sap pressure inside the xylem, sap-flow velocity, and xylem and phloem diameter changes. As environmental factors we measured VPD (vapour pressure deficit), and air, stem and soil temperature. At Tohmajärvi we also sampled stem and root material to analyse the patterns of carbohydrate status and relative water content. We measured 6 trees in Tohmajärvi and 1 in Hyytiälä.

Stem diameter changes, sap flow and sap pressure measurements

We measured the diameter changes in xylem and phloem with linear displacement transducers (using Solartron Inc., Model AX/5-0/5, Bognor Regis, West Sussex, UK; accuracy of 1 μm) in Hyytiälä, and model ZN11-T-WP Natkon, Oetwil am See, Switzerland in Tohmajärvi. Sap flow was measured with the Granier method from all the trees (Granier, 1987). The measurements were recorded every 10 minutes. Sap pressure was measured with a custom made lightweight differential pressure sensors. First a ~1 cm hole was drilled to the sapwood and in which the sensor was installed.

RESULTS

Sap pressure followed temperature and was inversely correlated with xylem diameter until the late stages of the sap exudation period (Fig. 1). During the last days of sap exudation period before sap pressure disappeared, sap pressure was negatively correlated with temperature and positively correlated with xylem diameter. Also, the maximum sap pressure measured during a given day correlated with the maximum xylem diameter that day (Fig. 2).
Figure 1. Fluctuations of xylem diameter changes (orange line in both graphs) and temperature (fig 1 a) in blue), and also xylem diameter changes and sap pressure (fig. 2 b) in grey).

Figure 2. Correlation factors of xylem diameter with temperature (in blue) and xylem diameter with sap pressure (in orange).
DISCUSSION

We hypothesize that two different processes are affecting sap pressure. First, increasing temperature increases the metabolic activity of sap pressurization. For example, the rate of water movement from the parenchyma cells to xylem vessels (causing sap pressurization) could increase with increasing temperature if the route of water movement is through aquaporins as aquaporin activity is known to increase with increasing temperature (e.g.). This hypothesis is also in line with the observation that xylem and phloem diameter (indicating water content of parenchyma cells), decreases when sap pressure increases. On the other hand, water evaporation through the bark and the developing buds increases with increasing temperature (due to its correlation with VPD), thus lowering sap pressure. It seems that the first process is dominating at the beginning of the period under observation, while the later is dominating at the end of the period, presumably because the developing buds start to transpire more.

We hypothesize that the positive relation between maximum daily sap pressure and the maximum daily xylem (and also whole stem) diameter occurs as days with high maximum xylem (and whole stem) diameter correspond to days when the parenchyma water content and turgor pressure are high to begin with in the morning and thus allows the generation of higher sap pressures.

CONCLUSIONS

In general, it seems that two factors are affecting water relations during the sap exudation period. Temperature increases metabolic activity which pressurizes the sap and refills embolism accumulated during the winter by yet an unknown mechanism, while VPD (highly correlated with temperature) increased the evaporation rate of water thus decreasing the sap pressure.

ACKNOWLEDGEMENTS

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REFERENCES

In situ cloud measurements in sub-arctic environment. The benchmarking of three cloud probes

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Keywords: CLOUDS, CCN, CLOUD PROBES, PALLAS.

INTRODUCTION

Atmospheric clouds are complicated systems which play a significant role in climate. Interactions between clouds and aerosols are associated with some of the largest uncertainties in predictions of climate change (IPCC, 2013). Many of the climatically important cloud properties (e.g. albedo, precipitation rate and lifetime) depend, amongst other factors, on the number concentration of aerosol particles and on their chemical composition (Komppula, 2005; Lihavainen, 2008).

Continuous, semi-long term, ground based, in-situ cloud measurements were conducted during the intensive Pallas Cloud Experiments (PaCE) in year 2013. The campaign focused on cloud and aerosols physico-chemical properties and their interactions. The measurements were conducted in Finnish sub-Arctic region at Sammaltunturi station (67°58’N, 24°07’E, 560 m a.s.l.), the part of Pallas Sodankyla - Global Atmosphere Watch (GAW) programme.

METHODS

The Sammaltunturi measurement site (67°58’N, 24°07’E, 560 m a.s.l.) located at a hill top and it was ~ 95 % of time inside a cloud during the campaign which allows direct measurements of aerosol-cloud interactions. However, the main motivation of this study was to focus on in-situ measurements of cloud properties with three different cloud probes and their mutual benchmarking.

A detailed analysis of all measured cloud microphysical properties was made and how they were influenced by meteorology was thoroughly investigated. We mutually compared and benchmarked performance of three cloud probes: the Cloud, Aerosol and Precipitation Spectrometer probe (CAPS), the Cloud Droplet Probe (CDP) and the Forward Scattering Spectrometer Probe (FSSP-100), all three made by DMT, Boulder, CO, USA. The FSSP and CDP probes were placed on a rotating platform, so that the inlet was always against the wind direction. The CAPS probe was fixed and heading the main wind direction at the station (NW) (Figure 1).
The presence of a cloud at the measurement site during this work was based on visibility. We considered that the station was inside a cloud while the horizontal visibility was less than 1000 meters, this was crosschecked against the cloud droplet count measured with cloud probes. In 2013 the period of the campaign was from 14 of September until 28 of November. From the total of 75 days, 64 days the station was inside a cloud for at least a part of the day. For the period when the station was inside a cloud, the temperature range was from -12 to 10 °C, the wind speed average was 7.30 (STD 2.8) m/s, the wind direction average was 172 (STD 75) degrees and the visibility average was 338.4 (STD 202.2) meters.

RESULTS

The main meteorological parameter that we used for comparing the cloud probes was the wind direction. We divided the three probes to two categories. Specifically, as probes that were installed on a rotating platform (FSSP-100, CDP) and probes which were installed on a non-rotating platform (CAPS). Regarding probes on a rotating platform FSSP-100 had the best data coverage (~ 95 %) in comparison with CDP which got usually frozen during night due to below zero temperatures and small opening of inhalation system, its data coverage was only ~ 65%. The intercomparison was made with Cloud and Aerosol Spectrometer (CAS_DPOL) from CAPS probe because it has similar size range with FSSP-100. As a result, we saw that the performance of CAPS cannot be considered as acceptable when the wind direction is perpendicular to fixed direction that the CAPS probe was installed (225 degrees) (Figure 2).

Figure 2. Left, number concentration minutes averages ratio of FSSP-100 to CAS_DPOL against the deviation from CAPS set point. The vertical red line indicates CAPS set point (~225 degrees). Right, the main wind direction that CAPS was installed is shown with blue colour.
There is also a clear connection with the wind direction which we can confirm by having a closer look to each cloud case. In 03.11.2013, the meteorological data show us that both of the two categories of the cloud probes have the same wind direction. (Figure 3).

Figure 3. Wind direction, wind speed and temperature at Pallas during 03.11.2013. From 00:00 until 14:00 the cloud probes have an agreement in wind direction.

This day indicates a clear case where all the probes have a good agreement in number concentrations. Also, the size distribution shows that all the probes the sizes similarly (Figure 4).

Figure 4. Left, number concentration of the three probes during 03.11.2013 is shown. The peak in count from 14:00 is a sign of probe freezing. Right, size distribution as measured by the three probes from 00:00 until 14:00.

In 29.10.2013 from 12:00 until 16:00, there is a deviation of about 60 degrees from the CAPS heading direction (225 deg). In that case, CAS_DPOL seems that has almost 60% of the FSSP-100 count. However, the size distribution in this time range shows that the losses are not size selective. (Figure 5).
CONCLUSIONS

This work indicates that the mutual direction of probe heading and wind direction plays a significant role, especially when the wind direction is perpendicular to the fixed direction of CAPS. However, it seems there are also other factors influencing the results. In general, rotational system with big opening of inhalation system would provide the best performance for in situ cloud measurements. The CDP probe often freezes in sub-zero condition, both the rotation and inhalation system because its big surfaces collecting ice and it has a small opening of inhalation system. CDP considered operating well for warm liquid clouds. The FSSP probe has the best data coverage from the three probes but it has relatively complicated data analyses. This means that several corrections have to be applied in FSSP data analysis. The CAPS probe has relatively good performance when wind direction is less than 60 degrees from the main wind direction. Some advantages of the CAPS probe is its extended size range and depolarization features which allow us to differentiate between water and ice.

ACKNOWLEDGEMENTS

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REFERENCES


EMULATION OF CLOUD-AEROSOL INDIRECT RADIATIVE EFFECTS (SA-ECLAIRE)

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Keywords: CLOUDS, INDIRECT RADIATIVE EFFECT, STATISTICAL EMULATION, ATMOSPHERIC MODELLING.

INTRODUCTION

Global climate models can neglect a lot of detail because of the coarseness of their grid spacing. One of the largest sources of uncertainty in global climate models is their treatment of clouds. Since clouds exist on length scales of metres to a few kilometres, and grid boxes in global models will often be a few hundred kilometres on a side, clouds cannot be explicitly represented.

Instead, clouds are represented by means of parameterisations based on average values of e.g. relative humidity over the whole grid box. Some brief simulations have been carried out at extremely high global resolution (Miyamoto et al., 2013), or implementing a two-dimensional cloud-resolving model within each grid box (Wang et al., 2011), but due to their computational expense, neither of these methods is suitable for standard use within global models at present.

A Gaussian-process statistical emulator would provide an efficient means to approximate the detail of cloud-resolving models within a much coarser global model, at minimal computational cost. However, this novel method includes its own distinct set of challenges.

METHODS

The Gaussian-process statistical emulator has several advantages over the more traditional parameterisation or even over a look-up table. By using smooth Gaussian functions to represent the model output and accounting for information from each of the training data points at every point in the parameter space, the emulator can be constructed using far fewer model simulations than a standard parameterisation. The emulator output also includes an uncertainty range for its estimate, and information on which input parameters have the greatest effect on the emulated values throughout the parameter space.

Look-up tables can also be used to store and retrieve output from a more complex model. The tabulated values can then be interpolated to estimate model output. However, constructing a look-up table requires running far more initial simulations, to fill the parameter space densely; and the interpolation will generally be linear and between nearest neighbours only (whereas the emulator implicitly contains information from more distant training data). For sufficiently large parameter spaces, the storage and retrieval of look-up table values can also be prohibitive.
We have used the UCLA Large Eddy Simulation model (UCLALES) to create the initial training data, and the R DiceKriging statistical package to construct a proof-of-concept emulator. The emulator estimates the cloud droplet number concentration (CDN, per kilogram of dry air) based on inputs of accumulation-mode aerosol number concentration (particles cm$^{-3}$), surface latent heat flux (Wm$^{-2}$), and magnitude of absolute humidity inversion (kg of water per kg of dry air). The initial training output data consists of domain-average CDN for the third hour of a three-hour simulation. Thirty simulations were carried out for the initial three-parameter example.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$N_{acc}$ (pcles cm$^{-3}$)</th>
<th>LHF (Wm$^{-2}$)</th>
<th>Δq (kg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>Maximum</td>
<td>1000</td>
<td>250</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Table 1. Range of parameters used to construct the proof-of-concept emulator of cloud droplet number concentration.

Construction of the emulator is straightforward, but validation must then be carried out using techniques described in (Olivier Roustant et al., 2012) and (Bastos and O’Hagan, 2009). The findings of this validation will be presented at FCOE. The next step will be to implement the emulator in the ECHAM-HAM-SALSA global climate model and use it to generate an estimate of the aerosol indirect radiative effect.

CONCLUSIONS

Gaussian process emulators have several advantages over traditional parameterisations and lookup tables, but face their own distinct set of implementation challenges. By constructing an emulator of cloud drop number concentration, as calculated by a cloud-resolving model, and implementing it in a global climate model, we intend to create an improved estimate of the aerosol indirect radiative effect with a minimal increase in computational cost.

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REFERENCES

ENHANCEMENT OF THE NUCLEATION FROM A-PINENE OZONOLYSIS IN THE PRESENCE OF DIMETHYLAMINE

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Keywords: Amines, Nucleation, Laboratory and Field Experiments, Mass Spectrometry

INTRODUCTION

Amines are emitted to the atmosphere from industry, combustion, biomass burning, animal husbandry and oceans (Ge et al., 2011). In addition, soil and vegetation act as important sources of amines, especially during periods with high biological activity (Ge et al., 2011). These compounds are ubiquitous in the atmosphere and observed in several locations in the world, for example Ge et al. (2011) summarized 154 identified amines in the atmosphere emitted from anthropogenic and biogenic sources. The most abundant amines in the atmosphere are low-molecular weight aliphatic amines such as methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA). Despite the high vapour pressures of low-molecular weight amines, they can affect the chemistry and lifecycle of atmospheric aerosols, especially due to their unique acid-neutralizing capacity. Therefore, some studies have highlighted the role of amines in the formation and growth of secondary aerosols (nucleation, secondary organic and inorganic aerosol mixtures) from laboratory experiments (Almeida et al., 2013; Erupë et al., 2011; Galloway et al., 2014; Tang et al., 2013) and field campaigns (Smith et al., 2010). Recent studies have demonstrated that in the atmosphere carbonyl compounds, such as glyoxal, methylglyoxal, glycoaldehyde or hydroxyacetone form N-containing and oligomeric compounds with small amines in aqueous aerosols (De Haan et al., 2010, Kua et al., 2011, Powelson et al., 2013, Galloway et al., 2014, Hawkins et al., 2014). More recently, laboratory and field studies have shown the formation of nitrogen-containing low volatile compounds from pinonaldehyde-dimethylamine reaction (Duporté et al., 2016), suggesting the potential role of amine on oxidation products of α-pinene in the atmosphere. In this context, the aim of this work was to investigate the effect of amines on the ozonolysis of α-pinene and to clarify the potential of these reactions in the formation and growth of secondary organic aerosols (SOAs).

METHODS

In this work, the reactivity experiments were performed in a flow tube reactor. The approach proposed here is based on the chemical analysis at the molecular level of both gaseous and particulate phase. Figure 1 presents the experimental set-up used in this work to investigate the effect of amines on the α-pinene ozonolysis reaction. The gas phase was on-line monitored by high resolution chemical ionization mass spectrometry (HR-LTOF-CIMS). Aerosol sampling was achieved using 47 mm PTFE filters at a flow rate of 1 L.min⁻¹. Structures of reaction products were determined by ultra-high-performance liquid chromatography coupled to electrospray liquid ionization Orbitrap mass spectrometry (UHPLC-HRMS). Particle size number distribution was measured with a scanning mobility particle sizer (SMPS). To support the results of laboratory experiments, ambient aerosol samples (PM₁) were collected from SMEAR II boreal forest site at Hyytiälä, Finland, during May-June 2016 and analysed by the same analytical methodologies.
CONCLUSIONS

Figure 2 presents the temporal profiles of selected ions by HR-LTOF-CIMS. Reactivity between oxidation reaction products of α-pinene, such as pinic acid and pinonic acid, and dimethylamine was observed. Surprisingly, a significant increase in the concentration of highly oxidized compounds (see C9H14O3I as an example in Figure 2) after injection of dimethylamine was also noticed in this work. Finally, nitrogen-containing reaction products were identified by HR-LTOF-CIMS (see C6H9NO3I as an example in Figure 2). Interestingly, a subsequent enhancement of the nucleation after α-pinene ozonolysis was seen in the presence of dimethylamine.

Figure 2. Temporal profiles of selected ions by HR-CIMS
In total, more than 40 nitrogen-containing compounds were identified from the filter samples in the presence of DMA by Orbitrap LC-MS. Furthermore, the presence of five reaction products (C_{11}H_{20}O_{2}N, C_{12}H_{15}NO, C_{11}H_{20}NO_{2}, C_{10}H_{17}NO_{3}, C_{12}H_{17}NO_{2}) in ambient SMEAR II aerosol samples was confirmed. MS² fragmentation patterns of m/z 198.1489 ions from α-pinene-O_{3}-dimethylamine experiments and PM_{1} sample in Hyytiälä are presented in Figure 3.

![Figure 3. MS² fragmentation pattern of m/z 198.148 ions detected (a) in α-pinene-O_{3}-DMA experiments and (b) PM_{1} sample in Hyytiälä (23.05.2016 day filter)](image)

Successful chemical characterization of gas- and particle- phases by high resolution MS techniques was performed in this work. New products were determined and identified for the first time and the reaction products found in ambient aerosol particles suggest that dimethylamine may play an important role in the formation and growth of SOAs after α-pinene ozonolysis in the atmosphere.

ACKNOWLEDGEMENTS

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REFERENCES


THE ROLE OF SLAC1-MEDIATED RAPID STOMATAL CLOSURE IN THE ECOPHYSIOLOGY OF PLANTS

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Keywords: STOMATA, POPULUS, SLAC1.

INTRODUCTION

The S-type anion channel SLAC1 (SLOW ANION CHANNEL-ASSOCIATED 1) has been shown to be responsible for rapid stomatal closure in response to various factors, such as light, reduced humidity, high CO2, ABA, H2O2, NO and Ca2+, in Arabidopsis thaliana (Vahisalu et al. 2003, Vahisalu et al. 2010). The molecular mechanisms of SLAC1 regulation have been extensively studied but more research is needed to understand its role in plant ecophysiology. The aim of this study is to understand the significance of SLAC1-dependent stomatal regulation under natural conditions with a special focus on tree species.

METHODS

We are elucidating the presence and structure of SLAC1 protein family and related stomatal functions in several plant species for which genome sequence information is available. In addition to the phylogenetic analysis, we are measuring stomatal sensitivities of several different species to different environmental factors such as CO2, humidity and light. This work is still ongoing and the aim is to link the variation in protein structure and conservation to the differences in stomatal regulation between various plant species.

CONCLUSIONS

Figure 1. Protein structures of the Arabidopsis SLAC1 orthologs in different plant species.
According to the phylogenetic analysis, the SLAC1 protein family members and their structures seem to be conserved among land plants. Especially, the SLAC1 anion channel has many evolutionally conserved structural domains. Interestingly, only *Populus* species seem to make an exception to this by having lost the functionally important features of SLAC1 (fig. 1). This together with the stomatal conductivity measurements suggest that *Populus* species may have lost the functionally important features of SLAC1 and thus have altered ability to regulate their stomatal aperture.

As a part of this project we have started this autumn a long term field experiment with transgenic hybrid aspen (Populus tremula x tremuloides). There are four different transgenic lines with potentially altered stomatal regulation. Two of these lines are knockout lines where the expression of *SLAC1* and its close homolog *SLAH3* (*SLAC1 HOMOLOGUE 3*) genes is prohibited using an RNAi technique and the other two lines express the Arabidopsis *SLAC1* gene with EYFP- or HA-protein tag. Currently, we are also conducting experiments with these lines in greenhouse conditions. These experiments together with the long term field study, will help us to unravel the ecophysiological role of the SLAC1 mediated fast stomatal closure and to understand why *Populus* species may have lost this mechanism.

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REFERENCES


NEW METHOD FOR DETERMINING THE RESPONSE TIME OF CONDENSATION PARTICLE COUNTER

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Keywords: RESPONSE TIME, PARTICLE COUNTER, SPARK GENERATOR.

INTRODUCTION

Numerous applications, such as rapid size scans, mobile applications and eddy covariance measurements require fast acting particle counters. The better the instrument time resolution is, the more information is possible to obtain from this kind of data. However, one must know the response of the instrument being used to accurately judge what time resolution is still suitable. This work describes how to determine accurately and precisely the response time of a particle counter using mostly typical aerosol instrumentation tools.

The determination of a particle counter response time is not as straightforward task as one might think, as there are numerous hidden caveats. For instance, the laminar flow profile within the instrument causes different response times for increasing and decreasing particle concentration, with the particle concentration decay being the slower of the two. This can lead to a situation, where the responses to changes in particle concentration increases are represented more accurately than the responses for concentration decays. This is the case for instance, when sampling particle concentrations at 1Hz with the TSI 3010 (Quant, 1992), a still widely used model.

The response time measurement methods, which are often not discussed in detail in the literature, but rather mentioned in passing, have been studied by a multitude of methods. Most of these works have used either valves (Quant et al. 1992; Hering et al. 2005), spark generators (Wang et al., 2002) or DMAs (Buzorius, 2001; Shi et al. 2005). Also ambient sampling (Wehner et al. 2011), and manual testing with applying a filter (Stolzenburg et al. 1991) have been used.

Besides the various testing methods, the terminology used has been widely varied. Different definitions for the words response time are being used; it is used in the literature to refer to the 95 % concentration change, the concentration change of τ, the change from 10 % to 90 % and the change from 0 – 98 %. The τ is among the most widely used parameters, which unfortunately is a parameter that does not immediately provide directly useful information for the CPSs end user. Hence, in this work the term response time shall refer to time corresponding to a 95 % change in the measured particle concentration, with respect to the concentration before the change occurred. This represent more closely a “true” change in the particle concentration from the point of view of the end user. Here we present a robust method, based on the valve control solution, for determining the response time of particle counters that should be viable for most existing particle counters.

METHODS

We tested different methods mentioned in the literature used in the determination of particle counter response time, in order to find the most suitable method for producing robust, and highly reproducible response times. The testing was done as a part of the development work of a new fast mixing type condensation particle counter.
The initial method tested was the method similar to that described by Buzorius (2001), in which DMA power control is used to rapidly move in and out of the voltage region that allows particles to pass the DMA. In this experiment, a short Vienna type DMA was used with 4 lpm aerosol flow and 20 lpm sheath flow. Right after the DMA outlet, there was an additional 9 lpm carrier flow added of particle free air that made the entire flow turbulent.

The second method tested was ambient sampling, along with manual filter usage. These both provided occasional sharp concentration changes, but too poor reproducibility to have any confidence in the results obtained. Hence the results of these methods are not shown here.

The third method was the use of a spark generator. The spark generator has been used at least by Wang et al. (2002) in the characterization of their mixing type particle counter. The spark generation of aerosols occurs when to electrodes with high voltage are brought close enough so that a spark discharge occurs. This produces a sharp pulse of particles, which then can be used to determine the response time.

The final method, which was found suitable, is a variation on valve method that used by Quant et al. (1991) and Hering et al. (2005). Unlike here, both Quant et al. and Hering et al. were sampling from ambient air. The setup used here is presented in Figure 1. The key differences with the previous implementations and the one used here is the generation of aerosol, as well as the high sheath flow rate used. Both additions are included to increase both the speed and the stability of the system. The sheath flow ensures turbulent conditions all the way to the instrument inlet and shortens considerably any potential flow distortions caused by the movement of the valve, while the use of the atomizer allows fine particle concentration control.

![Figure 1. CPC response time measurement set-up used.](image)

CONCLUSIONS

The results of these various response time measurement methods are illustrated in Fig 2. The figure shows the different measurements performed on the same fast mixing type particle counter developed in the University of Helsinki.
Figure 2. Observed response times for various response time determination set-ups.

The DMA method proved to have large residence times associated with it. The results could be improved by having a larger flow through the DMA as well as having a larger carrier flow. This however seemed to be quite unpromising approach, and based on the results presented in Figure 1 the approach was discarded in favour of faster alternatives.

The spark method on the other hand appeared to be a much more promising approach. However, closer inspection revealed the many caveats in the spark method. For instance, one cannot attain the concentration increase response accurately from spark measurement. The particle concentration increases very fast, but this largely due to the shape of the particle pulse, rather than the instruments true response. The pulse created is so transient, that the instrument does not ever reach the actual final concentration, but rather the concentration will start to decrease before the instrument reach the final value, only thus showing the steepest starting part of the instruments response. In theory, if the instrument is fast enough, the spark would be a suitable method, but this would require that the instruments response time would be around few milliseconds.

Also the spark generator is prone to produce extremely high particle concentrations, so that very large dilution is needed. If too high concentrations are used, the instrument underestimates the total particle number concentration due to coincidence. This leads to a false levelling out in the particle concentration prior to the instrument reaching the actual maximum particle concentration. Therefore it is suggested that moderate concentrations around 1000 - 5000 #/cm3 are used, in order to avoid the overestimation of the instruments speed.

However, if the spark is used in low enough concentrations the decay of the spark pulse is suitable for the instruments response time determination. Although the maximum of the actual concentration peak is not captured, the instrument observes some maximum value, and experiences concentration decay from that point at the same rate as from any other point. Here also, it still should be highlighted that too high concentration will lead to distortions in the response time determination. Here the coincidence will in fact act in the opposite manner, and distort the instruments response to appear slower than it is (see Fig. 2). This is caused by the fact that the coincidence will change the shape of the particle pulse, in affect widening the top of the pulse. This means that the particle decay will start apparently more slowly, than it does actually, and therefore create a false slow start to the process, as indicated in Fig. 3. Overall, the spark method can be used successfully for the response time measurements, but the user should be aware of the many potential sources of error with this method.
In contrast to the other methods here, the valve method is extremely simple when considering sources for error. The user has good control of the concentration and the flows, thus the problems coincidence and signal smearing in the tubing can be minimized. Furthermore, this method also allows one to determine the instrument’s response to a step change in both concentration increase and decrease, unlike the spark method. The main limiting factor of the method is the change time of the valve, which here was around 2 ms, which should still be small enough to be negligible for current CPCs. Based on the results gathered here, the valve method appears to be the most reliable method for determining the response time.

ACKNOWLEDGEMENTS

This work was supported by the Maj and Tor Nessling Foundation (grant 201600249), Academy of Finland Center of Excellence program (Center of Excellence in Atmospheric Sciences) and European Commission (ACTRIS2).

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INTRODUCTION

The photosynthetic sink of CO$_2$ described by gross primary production (GPP) is traditionally defined from direct eddy covariance (EC) measurements of CO$_2$ flux (NEE) taking into account respiration (R) defined from the nighttime data as

$$GPP_{res} = R - NEE$$

The problem with this method is the accurate determination of ecosystem respiration and more direct methods are needed. Carbonyl sulfide (COS) has been suggested to be a useful proxy for GPP since plants take up COS in a similar way as CO$_2$ via stomata (Wohlfahrt et al., 2012; Berry et al., 2013). In contrast to CO$_2$, there is no back-flux (respiration) of COS by plants and GPP can be calculated using equation

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

where $F_{COS}$ is the COS flux, LRU leaf-scale normalized ratio of COS to CO$_2$ assimilation rates and [CO$_2$] and [COS] concentrations of CO$_2$ and COS, respectively (Sandoval-Soto et al., 2005; Asaf et al., 2013). However, studies have found nocturnal uptake of COS at the ecosystem level (Billesbach et al., 2014) 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, CO$_2$, H$_2$O and CO mixing ratios (Kooijmans et al., 2016) and LI-6262 (LI-COR Inc., USA) analyzer for CO$_2$ and H$_2$O 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 profile above and within the canopy.

RESULTS

Preliminary results show nighttime ecosystem uptake of COS (negative flux) and a constant offset when comparing GPP$_{COS}$ and GPP derived from CO$_2$ measurements (GPP$_{res}$, Fig. 1). Soil chambers show constantly negative COS fluxes although there is no uptake of CO$_2$. Pine branches seem to be a sink of COS throughout the day indicating open stomata during nighttime. These findings show that negative ecosystem COS flux can be explained by incomplete stomatal closure during nighttime, and that soil brings a notable contribution to the ecosystem flux and it needs to be taken into account when calculating GPP$_{COS}$.

Figure 1. Diurnal cycles of GPP$_{COS}$ and GPP$_{res}$ measured with EC technique.
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. An offset between GPP calculated from CO₂ and COS flux measurements was found and it could be explained by soil contribution and incomplete stomatal closure during nighttime. Further examination of the data is still required to fully determine the contribution of each component.

ACKNOWLEDGEMENTS

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THE SOA FORMATION EFFICIENCY OF HEALTHY AND STRESSED SCOTs PINE EMISSIONS IS PRIMARILY CONTROLLED BY SESQUITERPENE EMISSION RATES

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Keywords: SECONDARY ORGANIC AEROSOL, BIOGENIC VOLATILE ORGANIC COMPOUNDS, CLIMATE CHANGE FEEDBACK.

INTRODUCTION

Plant emissions are a major source of biogenic volatile organic compounds (BVOCs) that lead to secondary organic aerosol (SOA) formation. Plants emit a diverse array of BVOCs, each with widely-varying potential for SOA formation. BVOC emission rates and the types of compounds emitted are controlled by a host of abiotic and biotic factors including temperature, light, and presence of disease or herbivores (Guenther et al., 1995; Niinemets et al., 2013, 2004). All of these are factors that are projected to change in the future. Consequently, there is a biosphere-atmosphere feedback that exists between i) climate change affecting plant emissions and ii) the SOA formed from those emissions impacting climate (Kulmala et al., 2004).

Initial estimates of this plant stress climate change feedback have demonstrated a negative feedback contributing to a climate forcing of -0.3 W m⁻² K⁻¹ whereby 1) warmer temperatures increase plant emissions 2) production of biogenic SOA mass and number concentration increases 3) the number of CCN increases causing a rise in cloud droplet number concentration and 4) the aerosol cooling effect is strengthened (Paasonen et al., 2013). This estimate was calculated based on changes to plant emissions due to temperature increases. However, studies using plant stress treatments associated with climate change impacts (i.e. drought, extreme temperature, herbivory, or a combination of these) have demonstrated that plant reactions to stress can be much more complex—inducing the emissions of new compounds not observed under non-stressed scenarios (Holopainen and Gershenzon, 2010). Furthermore, these changes to BVOC emission rates due to plant stress can impact the SOA formation potential of the plant emissions, either increasing or decreasing SOA yields depending on the types of emissions that are induced (Joutsensaari et al., 2015; Mentel et al., 2013). One plant stressor known to have a significant impact on plant emissions is increased presence of herbivores, and this climate change stressor is expected to be particularly strong in boreal regions (Netherer and Schopf, 2010). Thus a complete picture of climate change impacts on plant emissions and subsequent SOA formation remains unclear.
here are results from a laboratory study investigating the impact of bark borer pine weevils on secondary organic aerosol production from emissions of 7-year old Scots pines.

METHODS

Four experiments were conducted using a repeated measures experimental design where SOA formation efficiency from real Scots pine emissions was assessed during pre-treatment (baseline), active feeding, and post-treatment (herbivores removed) conditions. SOA was formed from plant emissions using an oxidation flow reactor (OFR) where plant volatiles were oxidized with OH radical. The OFR produced SOA with an equivalent photochemical age of approximately 1-2 days. This methodology provided measurements to directly link changes in plant emissions to SOA production. For each experiment, two plants were transported to the laboratory (one control and one treatment) where their foliage was placed in a dynamic Teflon enclosure and they were acclimated to laboratory conditions for 24 hours prior to the first SOA experiments. Baseline emissions and SOA production were investigated for a minimum of two days prior to treatment. The plant stress treatment was the application of four pine weevils (*Hyllobius abietis*) on each plant for two days. After herbivores were removed, the plant emissions and SOA production were monitored for at least five more days. The SOA experiments were conducted using the treatment plant before, during, and after herbivore treatment as the plant emission profile changed in response to the presence of the herbivores. Dilution air was added at the inlet of the OFR to actively control the concentration of BVOCs entering the flow tube reactor. This allowed us to calculate SOA mass yields across a range of organic aerosol concentrations during a single day and develop mass yield curves for different plant emission profiles. A summary of the instruments used in the laboratory investigation is provided in Table 1.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measurement</th>
<th>Data Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-Phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-MS-FID</td>
<td>Speciated Organics</td>
<td>Plant Emission Profiles</td>
</tr>
<tr>
<td>PTR-MS</td>
<td>Volatile Organic Compounds</td>
<td>Time series, ΔVOC for SOA Mass Yield Calc.</td>
</tr>
<tr>
<td>Particle-Phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMPS</td>
<td>Particle Size Distribution</td>
<td>Particle Number Concentration and Volume. Total organic aerosol (Coa) in SOA Mass Yield Calc.</td>
</tr>
<tr>
<td>HR-AMS</td>
<td>Composition</td>
<td>Herbivory Stress SOA Marker from PMF analysis</td>
</tr>
</tbody>
</table>

Table 1. A list of the instrumentation used during the laboratory investigation and their accompanying data products.

RESULTS & CONCLUSIONS

Plant volatile emissions increased during active feeding by pine weevils in each of the four experiments. Monoterpene emissions increased from an average of 50 +/- 10 μg m^-2 h^-1 before treatment to over 2000 +/- 380 μg m^-2 h^-1 during active feeding—an increase of over 4000%. This value was calculated from the average of all four experiments using the GC analysis results with the uncertainty range representing the standard deviation. After herbivores were removed, monoterpene emissions rapidly decreased with an average post-treatment emission rate of 435 +/- 140 μg m^-2 h^-1, which was still significantly higher than pre-treatment values (p<0.05, Mann-Whitney). Sesquiterpene emissions also increased significantly, but to a lesser extent than monoterpenes; average pre-treatment sesquiterpene emission rates were 15 +/- 3 μg m^-2 h^-1 before treatment to 31 +/- 8 μg m^-2 h^-1 during active feeding—an increase of approximately 100%. After treatment, sesquiterpene emission rates decreased to 18 +/- 5 μg m^-2 h^-1. Volatile emissions from the control plant did not increase. The monoterpene emission profile from control and treatment plants was dominated by less than 10 monoterpenoids, which constituted greater than 90% of the total monoterpenes emitted. These monoterpenoids included the following compounds listed in descending order of
contribution for the pre-treatment profile: α-pinene, p-cymene, d-3-carene, β-phellandrene, camphene, limonene, and β-myrcene.

SOA formation efficiency of the plant emissions was assessed by generating “Odum curves” (SOA mass yield vs. total organic aerosol mass) at a range of organic aerosol mass loadings before, during, and after herbivore treatment. Only the treatment plant emissions were used for the SOA generation experiments to link changes in SOA production to observed changes in the treatment plant emissions during the three experimental phases. SOA mass yield was calculated by dividing the total amount of organic aerosol mass generated in the flow tube by the mass of terpenoids (both monoterpenes and sesquiterpenes) that reacted. The PTR-ToF-MS was used to measure the reacted terpenoids by taking the difference between the outlet and inlet concentration of the OFR. At the gas-phase concentrations used in these experiments, all terpenoid compounds had completely reacted in the OFR. An SOA Odum curve was also generated using an α-pinene standard for comparison with the SOA generated from Scots pine emissions. In general, Scots pine emissions had higher SOA formation efficiency than α-pinene during the pre-treatment and post-treatment experimental phases. During active feeding, the SOA formation efficiency of Scots pine emissions decreased to the approximately the same level as pure α-pinene. For this particular herbivore, active feeding increased monoterpane emission rates much more than sesquiterpene emission rates (see previous paragraph). Consequently, the sesquiterpene-to-monomerene ratio (SQT:MT) substantially decreased from an average pre-treatment value of 0.3 to 0.015 during active feeding. When the SQT:MT increased after removing herbivores, the SOA formation efficiency increased to nearly the same level as pre-treatment values. These results highlight that sesquiterpenes, even in the small amounts observed pre- and post-treatment, play a significant role in SOA formation from a complex mixture of real plant emissions. It should be noted that other plant stressors (including other herbivores) can increase sesquiterpene emissions relative to monoterpane emissions. In those cases, the results presented here suggest that the stressed plant emissions would have higher SOA formation efficiency than the healthy plant emissions because the impact of plant stress on SOA formation will depend on the types of plant volatile emissions that are induced. For plants stressed by pine weevil herbivory, we observed two competing effects regarding SOA formation—plant volatile emission rates increased substantially, but the SOA formation efficiency of those emissions decreased. The next step required to evaluate the effect of pine weevil herbivory on SOA formation at the forest scale is to integrate these results into regional models. It is likely that the large increases in monoterpane emission rates after pine weevil herbivory would increase total SOA production and outweigh the decrease in SOA formation efficiency.

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INTRODUCTION

The portion of solar radiation that appears to originate from a small annulus around the Sun is called solar aureole or circumsolar radiation. This radiation arises from near-forward scattering of direct solar radiation by atmospheric particles with sizes comparable to or larger than the wavelength of sunlight (1 \( \mu \)m to 0.1 mm). Aureole radiation is widely detected by instruments measuring the direct radiation (i.e. pyrheliometers). Depending on the ambient atmospheric conditions, the near-forward scattered radiation can be a large portion of the total radiation measured by these instruments. This leads to overestimation of the amount of direct solar radiation. Especially in the presence of ice clouds, a considerably large part of the direct solar radiation is scattered into the aureole region, due to the strong forward peak in the scattering phase function of ice crystals. Therefore in the presence of ice clouds, retrieving the optical thickness or other properties of aerosols and/or clouds from the direct radiation measurements can be biased. For example, the performance of solar concentrating systems estimated based on pyrheliometer measurements is often systematically overestimated.

The amount of aureole radiation depends on the optical properties of the atmospheric particles such as the phase function, single scattering albedo and extinction coefficient. Furthermore, the volume averaged optical properties depend on the concentration and size-shape distribution of the particles. Although the role of the sizes and shapes of the ice-crystals on their optical properties has been studied in much detail, there is no detailed information on how the ice crystals affect the angular dependence of disk and aureole radiances.

In our ongoing study, we quantify the amount of diffuse radiances in the solar disk and around it at the opening angle of 16\(^\circ\) using a Monte Carlo radiative transfer model. In particular, the impact of size-shape distribution, concentration and roughness of the ice crystals as well as the impact of presence of aerosols on radiances is investigated. Input data for the model is based on in-situ
measurements of ice crystal shapes and sizes together with sounding and aerosol optical thickness data. The optical properties of individual ice crystals are obtained from a state-of-the-art database. In addition, the simulated radiances are compared against selected ground-based Sun and Aureole measurements, SAM.

<table>
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<tr>
<td>Time [UTC]</td>
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</tr>
<tr>
<td>$\theta_{sza}$ [°]</td>
<td>42.5-52.3</td>
</tr>
<tr>
<td>Cloud altitude [km]</td>
<td>8.0-11.5</td>
</tr>
<tr>
<td>$\tau_{aerosol}$ (AERONET)</td>
<td>0.166</td>
</tr>
<tr>
<td>$\tau_{cloud}$ (SAM)</td>
<td>0.3-3.2</td>
</tr>
</tbody>
</table>

Table 1: Flight information and measurement-based cloud (SAM, Sun and Aureole Measurements) and aerosol (AERONET) optical thicknesses, $\tau$, at 0.670 $\mu$m wavelength. $\theta_{sza}$ is the solar zenith angle during the flight.

METHODS

The downwelling monochromatic radiances at 0.670 $\mu$m are simulated using a modified version of the Monte Carlo model of the University of Kiel (MC-UniK) by Macke et al. (1999), which uses nontruncated treatment for the phase functions. The model is modified to account for the finite width of the solar disk (0.267° half opening angle) as well as the limb darkening effect. Thus, while the MC-UniK can account for three dimensional effects, the effect related to cloud horizontal inhomogeneity are not account for in this study. Mc-UniK outputs radiances [W/cm$^2$/sr/$\mu$m] as a function of angle from the center of the Sun out to 8°.

To be able to mimic naturally occurring vertical profiles of the optical properties of ice clouds (and atmospheric gases and aerosols) needed as input to the MC-UniK, measurement data obtained during the Atmospheric Radiation Measurement program’s 2010 Small Particles in Cirrus (SPARTICUS) field campaig are used. Ground-based measurements are obtained from the Southern Great Plains measurements site. The various ice cloud scenario studied are based on in-situ measured size distributions of ice clouds together with either measurement-based shape distributions or idealized single-habit distributions. In addition, three alternative representions of the concentrations of small ice crystals are used to test the sensitivity of the result to these highly uncertain concentration measurements of crystals with maximum size $D<100$ $\mu$m. To obtain the ensemble-averaged optical properties of the ice clouds, these size-shape distributions are combined with optical properties of individual ice crystals obtained from database of Yang et al. (2013). Due to the lack of measurement based information about surface roughness and other non-ideal features of ice particles, three different roughnesses are considered: completely smooth (homogeneous) (CS), moderately rough (MR) and severely rough (SR). Flight information on one example case is listed in Table 1.

RESULTS AND CONCLUSIONS

To demonstrate the impact of aerosol and cloud optical thicknesses on the radiances, Figure 1 shows the simulated radiances for a clear sky (gases only), cloud-free (gases and aerosols) and cloudy atmosphere (gases, aerosols and ice cloud). In the presence of the ice cloud the amount of aureole radance is orders of magnitude greater than in the cloud-free atmosphere. We found that the simulated radiances are most sensitive to the assumptions of ice crystal roughness, with ice crystal habit playing a somewhat smaller role. We noted that changes in the aerosol optical thickness affect
Figure 1: Impact of the clear sky, aerosols and cloud on the disk and aureole radiances as a function of angle from the center of the Sun. The cloud is described based on in-situ measured size-shape distributions of ice crystals with a maximum size larger than 100 μm.

the absolute values of the radiances, but not significantly the angular dependence. The differences between real direct radiation and that measured by a pyrheliometer come from the diffuse radiation at half opening angles smaller than around 3°. At this angular distance the radiances (with fixed cloud optical thickness, $\tau_{cloud}$) are most sensitive to the ice crystal roughness and concentration of small ice crystals.

Two examples of the comparison of the simulated and measured radiances are shown in Figure 2. For these simulations, the crystal concentrations are adjusted so that the simulated radiances are within 10% of the measured disk radiances. The resulting cloud optical thickness is different depending on whether smooth or roughened ice crystals are assumed and whether the small ice crystals are accounted for or not. Cloud optical thicknesses used in the simulations shown in Figure 2 are listed in Table 2. The cloud optical thickness tends to be smaller when the SR crystals are used instead of CS. The angular dependence for the severely rough ice crystals tends to mimic the measured radiances better than for smooth crystals as seen from Figure 2.

<table>
<thead>
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<th>$\theta_{sza}$ [$^\circ$]</th>
<th>50.4</th>
<th>50.0</th>
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<tbody>
<tr>
<td>$\tau_{cloud}$, SAM</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>$\tau_{cloud}$, SR, $N_3(D)$</td>
<td>0.5</td>
<td>1.0</td>
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<tr>
<td>$\tau_{cloud}$, CS, $N_3(D)$</td>
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<td>1.2</td>
</tr>
<tr>
<td>$\tau_{cloud}$, SR, $N_1(D)$</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>$\tau_{cloud}$, CS, $N_1(D)$</td>
<td>0.7</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 2: Two examples of the values of cloud optical thickness, $\tau_{cloud}$, used in the simulations with solar zenith angles of 50.4° and 50.0° for the size-shape distributions $N_1(D)$ and $N_3(D)$ of severely rough (SR) and completely smooth (CS) ice crystals. Cloud optical thicknesses retrieved from the Sun and Aureole measurements (SAM) at the same $\theta_{sza}$ are also shown.

To be able to mimic the disk and aureole radiances of an ice cloud, accurate information about the optical properties of the ice crystals is needed. Our version of the MC-UniK could be used in the future for analysing different cirrus cloud and aerosol scenarios and their effects on near-forward
Figure 2: Comparison of the simulated and ground measured radiances (hp and hn refer to Sun and Aureole measurements (SAM) on the right and left side of the Sun, respectively). Simulations are conducted using in-situ based size-shape distribution of either severaly rough (SR) or completely smooth (CS) ice crystals with (N$_3$(D)) or without (N$_1$(D)) contribution of crystals with maximum dimension smaller than 100 µm. For each size-shape distribution, the cloud optical thickness is adjusted so that the simulated disk radiances are within 10% of the measured disk radiances.

These unique modeling results might be of interest for concentrating power systems or instruments measuring direct (including aureole) and diffuse radiance. Our results indicate that the non-ideality of the ice crystals might be possible to retrieve from SAM measurements.

ACKNOWLEDGEMENTS

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SPRING RECOVERY AND VARIATION IN METHANE FLUXES FROM BOREAL TREES IN SOUTHERN FINLAND

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Keywords: METHANE FLUX, TREE, AERENCHYMA, TRANSPARATION.

INTRODUCTION

Methane (CH₄) is one of the most abundant greenhouse gases in the atmosphere (Hartmann et al. 2013). Boreal forests are generally considered as a net sink for atmospheric CH₄ due to the methanotrophic bacteria living in aerated soil layer (Topp and Pattey 1997; Kirschke et al. 2013). Plant species, such as sedges and rice, are capable of transporting microbially produced CH₄ from anaerobic soil conditions to the atmosphere (Nouchi et al. 1990; Greenup et al. 2000). Recent studies have revealed that alongside with above mentioned plants also trees are able to transport CH₄ from anaerobic conditions to the atmosphere (Terazawa et al. 2007; Rice et al. 2010; Gauci et al. 2010; Pangala et al. 2015; Machacova et al. 2016). This transport is hypothesized to happen actively in transpiration stream (Pangala et al. 2015; Machacova et al. 2016) or passively via aerenchymatic tissues (Terazawa et al. 2015). Furthermore, trees are noted to be possible independent sources of CH₄ from their leaves (Keppeler et al. 2006) and stems in aerobic conditions (Covey et al. 2012; Wang et al. 2016).

To date, the research of tree CH₄ fluxes covers principally tropical and temperate vegetation zones while studies in boreal forests are rare. In addition, high uncertainties remain in the mechanisms and the environmental factors behind the CH₄ emissions from trees. Research in boreal vegetation zone is urgently needed in order to obtain understanding of the magnitude and both spatial and temporal variability in tree CH₄ fluxes, and to study the contribution of trees to the ecosystem CH₄ fluxes. This study aims to estimate seasonal variation in CH₄ fluxes of boreal trees, and to assess the differences in fluxes between tree species, between growing habitats and in the vertical profile of the tree.

METHODS

We measured tree CH₄ fluxes during the beginning of the growing season (13.4.–13.6.2015) at SMEAR II station in Hyytiälä, southern Finland. The trees were selected from two sites with differing soil types, vegetation and forest structure. The first site was a small scale mesotrophic mire with c. 60 cm thick peat layer and water table depth in of 5–10 cm. At this site, Norway spruce (Picea abies) was the main tree species and downy birch (Betula pubescens) occurred as mixed species. The second site was situated in the middle of c. 50 years old Scots pine (Pinus sylvestris) stand on mineral soil where single birches occurred as mixed species.

The CH₄ fluxes were measured from downy birch and Norway spruce, both of which represent common boreal tree species growing in various habitats. Two birches and spruces were selected at the mire site and one birch at the pine stand site, and the flux measurements were performed at multiple tree stem heights and shoots. The fluxes were determined by using the closed static chamber technique (Pihlatie et al. 2013), and then up-scaled to tree CH₄ flux per hectare. Soil temperature, sap flow and soil moisture were measured to indicate the environmental factors that might regulate CH₄ fluxes. Moreover, external
meteorological data, such as precipitation, radiation and air temperature, available at SmartSMEAR\(^1\), was used in this investigation.

**RESULTS**

Methane was emitted both from the tree stems and from shoots. The emissions were in general higher from birches than from spruces. The measured flux also differed between birches growing in different sites, mire or on mineral soil. In the case of birch trees, the positive flux rates were considerably larger from the lower parts than the higher parts of the stems, and the emission rates from the lower parts tended to increase as the growing season proceeded (Figure 1). The shoot CH\(_4\) fluxes did not show distinct seasonal variation during the spring and early summer, and did not vary as much as the stem fluxes between the tree species or measurement sites. Furthermore, occasional CH\(_4\) uptake was observed in the shoots. Nevertheless, upscaling of tree CH\(_4\) fluxes, based on aboveground living biomass, showed greater emissions from the shoots than from the stems (Table 1).

At the mire plot, we found positive correlation between the stem CH\(_4\) fluxes of birches and soil temperatures \((r > 0.54, p < 0.05)\). Conversely, there was weak negative correlation between stem CH\(_4\) fluxes of the spruce trees and soil temperature at the mire site. Other environmental variables did not correlate with tree CH\(_4\) fluxes.

**CONCLUSIONS**

This study shows that trees living in the boreal region are capable to emit CH\(_4\) from their stems and shoots. However, the mechanisms still remain unidentified, as well as reasons for temporal and spatial variation in the CH\(_4\) flux between tree species. The large amount of living biomass in the shoots may be the main factor resulting in high CH\(_4\) emissions from tree gown in the upscaling. Thus, shoot fluxes have a potentially greater role in the tree CH\(_4\) dynamics compared to stems, and hence the shoot fluxes should be confirmed in future research. Transport mechanism of CH\(_4\) in tree might be the key to better understanding of tree mediated CH\(_4\) fluxes. Further research is needed to identify the differences between boreal tree species in the capability of transporting CH\(_4\) from the soil to the atmosphere, and to differentiate between CH\(_4\) transport from the soil and *in situ* production of CH\(_4\) within a tree.

Figure 1. Downy birch CH\(_4\) fluxes at the beginning of the growing season from the lowest parts of the stems.

\(^1\) http://avaa.tdata.fi/web/smart
<table>
<thead>
<tr>
<th>Soil type</th>
<th>Species</th>
<th>Stem CH₄ flux (g ha⁻¹ d⁻¹)</th>
<th>Shoot CH₄ flux (g ha⁻¹ d⁻¹)</th>
<th>Tree CH₄ flux (g ha⁻¹ d⁻¹)</th>
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<tr>
<td>Mire</td>
<td>B. pubescens</td>
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<td>1.32</td>
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<tr>
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<tr>
<td>Mineral</td>
<td>B. pubescens</td>
<td>-0.023</td>
<td>2.44</td>
<td>2.42</td>
</tr>
</tbody>
</table>

Table 1. Upscaled CH₄ fluxes from trees to forest level by soil types and species.

ACKNOWLEDGEMENTS

This work was supported by the Emil Aaltonen Foundation, Academy of Finland (272091, 292699, 294088, 288494), National Centre of Excellence (272041), ICOS-FINLAND (281255), the project ENVIMET (CZ.1.07/2.3.00/20.0246) and the National Programme for Sustainability I (LO1415).

REFERENCES


TERPENOID, ACETONE AND ALDEHYDE EMISSIONS FROM NORWAY SPRUCE

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INTRODUCTION

Vegetation produces and emits vast amounts of biogenic volatile organic compounds (VOCs), especially in the densely forested boreal regions (Hakola et al., 2001, 2006; Tarvainen et al., 2005), which are mainly monoterpenes (MT), sesquiterpenes (SQT) and oxygenated volatile organic compounds (OVOCs). In the atmosphere these compounds are oxidized, affecting tropospheric ozone formation (Chameides et al., 1992) and influencing the lifetime of methane. In addition reaction products of VOCs also participate in the formation and growth of new particles (Tunved et al., 2006). In smog chamber studies secondary organic aerosol (SOA) yields for different hydrocarbons and even for different monoterpenes have been found to vary considerably (Griffin et al., 1999). Jaoui et al. (2013) studied SOA formation from SQT and found that the high reactivity of SQT resulted generally in high conversion into SOA products. Furthermore, they found that the yields were dependent on the oxidant used and were highest for nitrate radical ($\text{NO}_3^-$) reactions. Of the sesquiterpene acidic products, only $\beta$-caryophyllinic acid has been observed in ambient samples (Jaoui et al., 2013; Vestenius et al., 2014). Due to their high reactivity, SQT are not usually found in ambient air. Hakola et al. (2012) detected longifolene and isolongifolene in boreal forest air during late summer. Hence, the best way to evaluate the atmospheric impact of sesquiterpenes is to measure them from emissions. In addition to detection of individual monoterpenes gas-chromatograph mass-spectrometer (GC-MS) allows sensitive detection of sesquiterpenes, which is often difficult to perform under field conditions. The on-line measurements were considered essential for evaluating the factors affecting emission rates, for example their temperature and light dependence. Our campaigns cover periods of years 2012, 2014 and 2015 during spring and summer, altogether about 14 weeks. In 2015 also carbonyl compounds were added to the measurement scheme, since there is no earlier data of their emissions.

In the present study we conducted on-line gas-chromatographic measurements of emissions of mono- and sesquiterpenes as well as $\text{C}_4$-$\text{C}_{10}$ saturated aliphatic carbonyls from Norway spruce (Picea abies L. Karst) branches. Although Norway spruce is one of the main forest tree species in Central and Northern Europe, there are relatively few data on its emissions (Hakola et al., 2003; Grabmer et al., 2006; Bourtsoukidis et al., 2014a and b, Yassaa et al. 2012). In addition to detection of individual monoterpenes gas-chromatograph mass-spectrometer (GC-MS) allows sensitive detection of sesquiterpenes, which is often difficult to perform under field conditions. The on-line measurements were considered essential for evaluating the factors affecting emission rates, for example their temperature and light dependence. Our campaigns cover periods of years 2012, 2014 and 2015 during spring and summer, altogether about 14 weeks. In 2015 also carbonyl compounds were added to the measurement scheme, since there is no earlier data of their emissions.
METHODS

The measurements were conducted at the SMEAR II station in 2011, 2014, and 2015. The measurements took place in spring/early summer 2011 (two weeks in April, five days in May and three days in June), spring/summer 2014 (one week in May, two weeks in June and one week in July), and summer 2015 (one week in June and two weeks in August).

The selected trees were growing in a managed mixed conifer forest (average tree age ca 50 years), and located about 5 meters from the measurement container. The height of the tree in 2011 was about 10 meters. The samples were collected at a height of about 2 meters from a fully sunlit, healthy lower canopy branch pointing towards a small opening. In 2014 and 2015 a younger tree (ca. 1 m tall, age ca 15 years) about 5 meters away from the tree used in 2011 was selected for the study. The branches were placed in a Teflon enclosure and the emission rates were measured using a dynamic flow through technique. The emission rates were measured using an on-line gas-chromatograph-mass-spectrometer. VOCs from a 40-60 ml/min subsample were collected in the cold trap of a thermal desorption unit (Perkin Elmer ATD-400) packed with Tenax TA in 2011 and Tenax TA/Carbopack-B in 2014 and 2015. The trap material was changed since isoprene was found not to be retained fully in the cold trap in 2011. The trap was kept at 20°C during sampling to prevent water vapour present in the air from accumulating into the trap. This allowed the analysis of mono- and sesquiterpenes. The thermal desorption instrument was connected to a gas chromatograph (HP 5890) with DB-1 column (60 m, i.d. 0.25 mm, f.t. 0.25 µm) and a mass selective detector (HP 5972). One 20-minutes sample was collected every other hour. The system was calibrated using liquid standards in methanol injected on Tenax TA-Carbopack B adsorbent tubes. We had no standard for sabinene and therefore it was quantified using the calibration curve of β-pinene. The detection limit was below 1 ppt for all mono- and sesquiterpenes. The following compounds were included in the calibration solutions: 2-methyl-3-buten-2-ol (MBO), camphene, 3-carene, p-cymene, 1,8-cineol, limonene, linalool, myrcene, α-pinene, β-pinene, terpinolene, bornylacetate, longicyclene, isolongifolene, β-caryophyllene, aromadendrene, α-humulene, β-farnesene. Isoprene was calibrated using gaseous standard from NPL (National Physical Laboratory). Compared to off-line adsorbent methods this in situ GC-MS had clearly lower background for carbonyl compounds and in 2015 we were able to measure also acetone and C₄-C₁₀ aldehyde emission rates. The aldehydes included in the calibration solutions were: butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal. Unfortunately, acetone co-eluted with propanal and the calibration was not linear due to high acetone background in adsorbent tubes used for calibrations.

The emission rate is determined as the mass of compound per needle dry weight and time according to

\[ E = \frac{(C_2 - C_1)F}{m} \]  

Here \( C_2 \) is the concentration in the outgoing air, \( C_1 \) is the concentration in the inlet air, and \( F \) is the flow rate into the enclosure. The dry weight of the biomass (\( m \)) was determined by drying the needles at 75 °C for 24 hours.

RESULTS AND DISCUSSION

Since most of the emission rates of the measured compounds were higher in late summer than in early season, we calculated the spring (April and May), early summer (June to mid-July) and late summer (late July and August) mean emissions separately. This described the emission rate changes better than monthly means. Seasonal mean emission rates of isoprene, 2-methyl-3-buten-2-ol (MBO), monoterpenes (MT) and sesquiterpenes (SQT) are presented in Table 3 and typical diurnal variations of the most abundant compounds for each season are shown in Fig. 1.

Norway spruce is known to be a low isoprene emitter and a moderate monoterpenes emitter (Kesselmeir and Staudt, 1999; Grabmer et al., 2006; Bourtsoukidis et al., 2014a, b). Our study confirmed these earlier results,
although the seasonal pattern of emissions was clearly different. Isoprene emission rates were low early summer, but increased towards August and late summer mean emission rate was 6 ng g(dry weight)\(^{-1}\) h\(^{-1}\). The highest daily maxima isoprene emissions were about 70-80 ng g(dw)\(^{-1}\) h\(^{-1}\), but usually they remained below 20 ng g(dw)\(^{-1}\) h\(^{-1}\). MBO emission rates were even lower than isoprene, the late summer mean was 2.4 ng g(dw)\(^{-1}\) h\(^{-1}\). MT emission rates were also low in April, May and still in the beginning of June for every measurement year, below 50 ng g(dw)\(^{-1}\) h\(^{-1}\) most of the time. At the end of June the MT emission rates started to increase (about 30 %) to the level where they remained until the end of August, the sum of MT daily maxima still remaining below 300 ng g(dw)\(^{-1}\) h\(^{-1}\).

A substantial change in the emission patterns took place at the end of July, when SQT emission rates increased up to 3-4 times higher than the MT emission rates at the same time (Table 3). Such a change in emissions was not observed in a study done in a spruce forest in Germany by Bourtsoukidis et al. (2014b). Instead of late summer increase especially in SQT emissions (in our data from 0 to 84 ng g(dw)\(^{-1}\) h\(^{-1}\)), they observed highest MT and SQT emissions already during the spring (203 and 119 ng g(dw)\(^{-1}\) h\(^{-1}\), respectively) after which emissions significantly declined, median MT emissions being 136 and 80 ng g(dw)\(^{-1}\) h\(^{-1}\) and SQT emissions 65 and 21 ng g(dw)\(^{-1}\) h\(^{-1}\) during summer and autumn, respectively. Further, they report that monoterpenes dominated the Norway spruce emissions through the entire measuring period (April-November), SQT emission rates being equal to MT emission rates during spring, but only about half of MT emission rates during summer and about 20 % during autumn. One potential explanation for such a different seasonality may lie in the differences between site specific factors such as soil moisture conditions, local climate, stand age or stress factors. In a boreal forest, late summer normally is the warmest and most humid season favouring high emissions, as was also the case in our study periods. On the contrary, in central Germany July was relatively cold and wet, and according to the authors, reduced emissions were therefore not surprising (Bourtsoukidis et al 2014b).

Another interesting feature resides in the specified emission rates of different compounds. In the current study the main SQT in spruce emissions was β-farnesene. About 50% of the SQT emission consisted of β-farnesene and its maximum emission rate (155 ng g(dw)\(^{-1}\) h\(^{-1}\)) was measured on the afternoon of 31 July 2015. Two other SQTs also contributed significantly to the total SQT emission rates, but since we did not have standards for these other SQT, their quantification is only tentative. Linalool emissions increased simultaneously with SQT emissions, in the same way as was previously observed in the measurements of Scots pine emissions in the same forest in southern Finland (Hakola et al., 2006), where emissions were found to increase late summer concomitant with the maximum concentration of the airborne pathogen spores, and Hakola et al. (2006) suggested a potential defensive role of the conifer SQT emissions. Several other reports point to similar correlations between SQT (in particular β-farnesene) and oxygenated monoterpenes such as linalool emissions and biotic stresses in controlled experiments. For example, increases in β-farnesene, methyl salicylate (MeSA) and linalool emissions were reported to be an induced response by Norway spruce seedlings to feeding damage by mite species (Kännaste et al. 2009), indicating that their biosynthesis might prevent the trees from being damaged. Interestingly, the release of (E)-β-farnesene seemed to be mite specific and attractive to pine weevils, whereas linalool and MeSA were deterrents. Blande et al. (2009) discovered pine weevil feeding to clearly induce the emission of monoterpenes and sesquiterpenes, particularly linalool and (E)-β-farnesene, from branch tips of Norway spruce seedlings. Also, in a licentiate thesis of Pettersson (2007) linalool and β-farnesene were shown to be emitted due to stress. The emissions from Norway spruce increased significantly after trees were treated with methyljasmonate (MeJA). Martin et al (2003) discovered that MeJA triggered increases in the rate of linalool emission more than 100-fold and that of sesquiterpenes more than 30-fold. Emissions followed a pronounced diurnal rhythm with the maximum amount released during the light period, suggesting that they are induced de novo after treatment. Our study shows that such major changes in emission patterns can also occur in mature trees in field conditions, and without any clear visible infestations or feeding, indicating that they probably are systemic defence mechanisms rather than direct ones (Eyles et al 2010).

In 2015 we measured also acetone and C\(_6\)-C\(_{10}\) aldehyde emission rates. The total amount of the measured carbonyl compounds was comparable to the amount of monoterpenes (Table 3) although with our method
it was not possible to measure emissions of the most volatile aldehydes, formaldehyde and acetaldehyde, which are also emitted from trees in significant quantities (Cojocariu et al., 2004, Koppmann and Wildt, 2007; Bourtsoukidis et al., 2014b). The carbonyl compounds consisted mainly of acetone (30 %), and the shares of nonanal (21%), decanal (17%), heptanal (14%), hexanal (10%) and pentanal (5%). The shares of butanal and octanal were less than 2% each. Many reports show that the short-chained oxygenated compounds such as aldehydes are effectively released but also absorbed by the vegetation especially when it is moist (e.g. Karl et al., 2005, Seco et al., 2007).

<table>
<thead>
<tr>
<th></th>
<th>spring (337)</th>
<th>early summer (534)</th>
<th>late summer (159)</th>
</tr>
</thead>
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<tr>
<td>Isoprene</td>
<td>bdl</td>
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<tr>
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<td>β-Pinene</td>
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<td>Linalool</td>
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</tr>
<tr>
<td>Decanal</td>
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</table>

Table 1. Seasonal mean emission rates of isoprene, 2-methylbutenol (MBO), MT, SQT, acetone and C4-C10 carbonyls in ng g(dw)^{-1} h^{-1}. “na” means that the compounds were not included in the analysis. Spring is April-May, early summer 1.6-15.7 and late summer 16.7-31.8. bdl = below detection limit. Values are averages for the three measurement years (2011, 2014, 2015). Other SQT = sum of all other sesquiterpenes in emissions. The number of the measurements each season is in parentheses.
Figure 1. Variability of the most abundant emitted compounds in each season. Aldehydes are sum of all C_2-C_{10} carbonyls.
ACKNOWLEDGEMENTS

The financial support by the Academy of Finland Centre of Excellence program (project no 272041) is gratefully acknowledged.

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COMPARISON OF THE ABOVE CANOPY AND THE FOREST FLOOR METHANE FLUX MODELLLED BY SOIL WATER CONTENT

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Keywords: METHANE EMISSIONS, LIDAR, MODELLING.

INTRODUCTION

Methane (CH$_4$) is among the most important greenhouse gases and its atmospheric concentration is rising (Hartmann et al., 2013). Boreal upland forests are traditionally considered as an important CH$_4$ sink due to CH$_4$ oxidation in the soil (Kirschke et al., 2013). However, aerated soils may also be habitats of CH$_4$ producing microbes (Angel et al., 2012), and thus the upland soils have a capacity to emit CH$_4$, when soil moisture is at adequate level (Sjögersten and Wookey, 2002; Matson et al., 2009; Shoemaker et al., 2014).

Furthermore, vegetation has been found to contribute to the ecosystem-atmosphere CH$_4$ exchange. Trees have been discovered to be capable of transporting CH$_4$ produced in the anaerobic soil conditions to the atmosphere (e.g. Rusch and Rennenberg 1998; Gauci et al., 2010; Machacova et al., 2016).

Nevertheless, the sources and the mechanisms of the observed CH$_4$ emissions from the forests are still mostly unknown. Airborne lidar (light detection and ranging) technique is an active remote sensing method that can be used to observe the vegetation and terrain, and which is very effective in forests (Korpela et al., 2009). By utilising lidar data and in situ measurements of CH$_4$ fluxes, our aim is to model the potential CH$_4$ flux of a boreal forest floor.

METHODS

We have conducted CH$_4$ flux measurements at SMEAR II station in Hyytiälä (61° 51’ N, 24°17’ E; 181 m asl), southern Finland since 2012 at different scales. Above the canopy flux measurements have been operative since the beginning of 2012 using concentration gradient method (Peltola et al., 2012). Forest floor CH$_4$ flux measurements have been performed using the static chamber method during the summer 2013 and 2014 from 54 locations in the footprint area of the above canopy flux measurements, and in addition from selected locations approximately every month from October 2014 to June 2015.

In addition to the CH$_4$ flux measurements, soil volumetric water content (VWC) next to the soil chambers has been measured every time simultaneously with the forest floor flux measurements. Moreover, in order to get wider understanding of the interannual change in the soil moisture conditions, the soil VWC was measured next to all the soil chamber locations three times in summer 2016. In order to model forest floor CH$_4$ fluxes at ecosystem level, we have tested whether it is possible to predict the soil moisture conditions by using local elevation (the elevation of the location vs. the ground elevation ± 20 m around the location), slope and ground return intensity (GRI) calculated from the lidar data (National Land Survey of Finland). We categorised the 54 flux measurement locations into four classes based on the soil VWC measurements: (1) the locations where the VWC is always less than 0.3 m$^3$ m$^{-3}$, (2) the VWC always less than 0.5 m$^3$ m$^{-3}$ and the locations where any of the measurements is above 0.3 m$^3$ m$^{-3}$, (3) the VWC always less than 0.8 m$^3$ m$^{-3}$ and any of the measurements above 0.5 m$^3$ m$^{-3}$, and (4) the locations where any of the measurements shows VWC above 0.8 m$^3$ m$^{-3}$. Thus the locations where there is potential for CH$_4$ emissions are in group 4.
After that, we explored how the different properties of the landscape calculated from the lidar data vary within these classes. Similar type of method has been used previously for classification of mire site and vegetation types (Korpela et al., 2009). Furthermore, based on the statistically significant correlation between the forest floor CH$_4$ fluxes and the soil moisture ($r = 0.30$, $p < 0.001$), we build a simple model to estimate CH$_4$ fluxes from the forest floor. In the end, the potential forest floor CH$_4$ flux will be compared to the measured above canopy CH$_4$ flux.

RESULTS

The above canopy measurements have indicated occasional small CH$_4$ emissions. In addition, the soil chamber measurements have demonstrated that there are a few locations at the footprint area that are able to emit significant amounts of CH$_4$. In order to confirm the emissions from above the canopy, the ecosystem scale CH$_4$ flux is currently measured with eddy covariance (EC) method since the summer 2016.

DISCUSSION AND CONCLUSIONS

The modelled map of the potential CH$_4$ flux from the forest area around the flux measurement mast shows the potential sites of CH$_4$ emissions (Fig. 1). The map is consistent with the four classes based on the soil moisture indicating that drier areas have potential for CH$_4$ uptake while the wet areas have emission potential. The known wet locations are indicating high potential CH$_4$ emissions (illustrated with red in the map), although also the road is interpreted as wet area, and thus some adjustment of the method is still needed. The method is promising, and it will be used to compare the modelled forest floor and the measured ecosystem scale CH$_4$ fluxes.

![Figure 1: Potential CH$_4$ flux at the SMEAR II site based on the modelled soil moisture. The blue areas show potential uptake and the red areas show potential emissions of CH$_4$, while the white areas indicate flux close to zero. The blue circle is the main measurement mast of the station, and the red circles are the soil chamber locations.](image-url)
ACKNOWLEDGEMENTS

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REFERENCES


EFFECTS OF BOUNDARY LAYER DYNAMICS ON AEROSOL COMPOSITION DURING NEW PARTICLERS FORMATION EVENTS

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Keywords: PLANETARY BOUNDARY LAYER, NUCLEATION, SP-AMS.

INTRODUCTION

Nucleation events are frequently observed on a global scale (Kulmala et al., 2004). New particle formation depends on the gas-phase species emitted and their subsequent processing in the atmosphere. When emitted at the land surface, they enter into the planetary boundary layer (PBL), which is characterized by strong turbulent motions that are largely influenced by the underlying land surface and the free troposphere on top of it. PBL dynamics affect the processing the aerosol precursor species and the partitioning into the aerosol phase of their low-volatility reaction products.

This study presents results of the effect of air dynamics and atmospheric chemical reactions on the observed aerosol composition measured by aerosol mass spectrometer during nucleation events in Hyytiälä, Finland.

METHODS

The measurements were carried out at Station for Measuring Forest Ecosystem-Aerosol Relations (SMEAR II) in Hyytiälä forestlands in Southern Finland (61° 51’N, 24° 17’E) during 2\textsuperscript{nd} April—10\textsuperscript{th} July, 2014 (Hari and Kulmala, 2005). Real-time measurements of particle chemical composition were conducted using a soot particle aerosol mass spectrometer (SP-AMS) (Onasch et al., 2012). During the campaign, SP-AMS was operated at 5-min saving cycles alternatively switching between SP-mode and EI-mode. In SP-mode, AMS was operated with both intracavity laser vaporizer and the standard tungsten vaporizer to produce mass spectra of laser-light absorbing particles such as refractory black carbon (BC) and non-refractory species. In EI-mode, only the tungsten vaporizer was used to measure non-refractory chemical species.
Concentrations of sulfate acid (H$_2$SO$_4$) and extremely low volatility organic compounds (ELVOCs) were measured by a chemical ionization time-of-flight mass spectrometer (CI-Tof-MS) (Ehn et al., 2014; Jokinen et al., 2015). The CI-MS was run in the negative ion mode with NO$_3^-$ acting as the reagent ions. The gas VOCs were monitored by a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) (Ionicon Analytik GmbH, Jordan et al., 2009).

The height of planetary boundary layer (PBL) at the measurement site was provided by HYSPLIT (Draxler and Rolph, 2013). The modelled PBL data was also validated against the measurements by a Radiosonde.

The aerosol number concentration and size distributions in a size range of 10-800 nm were measured by a Differential Mobility Particle Sizer (DMPS). Other supporting particle-phase and gas-phase measurement includes O$_3$, SO$_2$, CO, NO$_x$ and meteorological parameters (wind speed, wind direction, precipitation, temperature, solar radiation and relative humidity) that are recorded continuously at the site throughout the year, details of which are described by Junninen et al. (2009).

RESULTS AND CONCLUSIONS

Totally, five new particle formation events were selected (Table 1). All the events lie in the first half campaign time in the Finish Spring time when the nucleation event frequently takes place. For each event, the time covers the successive periods before and after nucleation moments for the purpose of exhibition of an overall picture of evolution of chemical composition throughout the new particle formation event. On average, the aerosol mass concentration during the five events was 1.0 μg m$^{-3}$, which was one-third of the average value of the whole campaign. Concerning the chemical composition, organic component accounted for 58.5 %, sulfate 24.0 %, ammonium 7.3 %, nitrate 3.1 %, black carbon 6.3 % and chloride < 1 % of the total PM1 mass, respectively.

<table>
<thead>
<tr>
<th>Nucleation Number</th>
<th>Time periods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start</td>
</tr>
<tr>
<td>E0804</td>
<td>01:01 08/04/2014</td>
</tr>
<tr>
<td>E1504</td>
<td>11:35 15/04/2014</td>
</tr>
<tr>
<td>E2304</td>
<td>05:40 23/04/2014</td>
</tr>
<tr>
<td>E2904</td>
<td>04:04 29/04/2014</td>
</tr>
<tr>
<td>E0305</td>
<td>06:24 03/05/2014</td>
</tr>
</tbody>
</table>

Table 1. The number sequence, time period, the mass concentrations of aerosol species during the new particle formation events that the study focuses on.

The size distributions, time series of aerosol components, and meteorological parameters during nucleation events in this campaign are shown in Figure 1. Firstly, we have systematically observed decrease of organic and sulfate aerosols in the measured mass concentrations. Secondly, we also observed a faster decrease rate of organic mass concentration than sulfate before the nucleation events (light pink bars, Panel D, Fig. 1). As a result, the mass fraction of sulfate to total aerosol mass increased, in contrast to a distinct decrease of organic fraction (light pink bars, Panel E, Fig. 1). The rapid decrease of aerosol concentrations was coinciding with the rising of PBL height when the sunrise starts in morning hours (refer to Fig. 2). The wind speed and wind direction were relatively constant before nucleation. Hence, the observed decrease of aerosol mass is firstly interpreted by a dilution effect on the aerosol concentrations due to the vertical air mass exchange with the development of PBL height. As a closer view, the
development of PBL height coincided with the decreased aerosol mass as the UV radiation intensity strengthens. The height of boundary layer was then converted to dilution factors as a function of time. The time series of measured organic and sulfate mass concentrations and theoretical ones were shown in Fig. 2. The theoretical mass concentrations were calculated upon an assumption that the change of aerosol concentrations was controlled only by PBL height (multiplied by dilution factors). We have seen that the patterns of theoretical values were following the measured ones for both organic and sulfate species: during the night, the aerosol particles were concentrated in the shallow boundary layer. In next morning when the PBL grows, air from free troposphere with a lower background aerosol concentration is entrained and mixed with the old aerosol population in PBL, leading to a decrease in the measured aerosol mass. However, the modelled aerosol concentrations were much smaller for sulfate and organic than the measured ones, suggesting the above mentioned dilution theory leads to an over-interpretation to the measurement data and other mechanisms also affected those two aerosol species.

Figure 1. Observation of new particle formation events in E0305 during the campaign. Panel A: aerosol number size distributions from DMPS; Panel B: volume size distributions; Panel C: aerosol total number concentration; Panel D: mass concentrations of organic (green) and sulfate (red) species by AMS; Panel E: mass fraction of organic and sulfate to total aerosol mass concentration; Panel F: mass fraction of LVOOA and SVOOA to total organic mass concentration; Panel G: O:C ratio of organic species by AMS; Panel H: wind speed and direction.
CONCLUSIONS

Even considering the efficient measurement of particle size range in the accumulation mode by AMS, we observed the relative change of chemical composition of aerosol particles when the atmospheric nucleation events start. In the morning hours, the entrained background sulfate aerosols in the air mass vertical convection accounted mainly for an increase of sulfate mass fraction and atmospheric chemistry plays a negligible role in interpreting the results. For organic aerosols, condensation of organic vapor from the atmospheric chemistry plays a role in affecting the relative aerosol composition during the air dynamics. The fact that higher sulfate mass fraction than organic demonstrated that aerosol entrainment from free troposphere in this campaign played a more important role in affecting the aerosol composition than atmospheric chemistry in the beginning of nucleation events.

ACKNOWLEDGEMENTS

The financial support by the Academy of Finland Centre of Excellence program (decision no. 272041), academy of Finland (259005), European Research Council (Starting Grant 355478), and UEF Postdoc Research Foundation (930275) is gratefully acknowledged.

REFERENCES


ON THE FORMATION MECHANISM OF HIO$_3$

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Keywords: IODIC ACID, NUCLEATION, CLUSTER FORMATION, ANTARCTICA.

INTRODUCTION

Homogeneous nucleation and sequential cluster growth via HIO$_3$ addition were recently discovered to be important over coastal areas (Sipilä et al., 2016). However, two questions remain. The first one is the role of HIO$_3$ in places other than coastal areas. Data from Mace Head, Hyytiälä and Antarctica were analysed to get an idea of the concentration of HIO$_3$ over these regions. The second one is the formation mechanism of the HIO$_3$ in ambient environment. Two formation pathways were proposed by quantum chemistry calculation: one suggested that reaction R1 can form HIO$_3$ (Drougas & Kosmas, 2005), while the other proposed that the reaction R2 forms HIO$_3$ (Plane et al., 2006). However, no dedicated experiment was conducted to confirm these calculations. Here, we present the first experimental evidence which suggests that the reaction between OIO and OH is a more efficient pathway to form HIO$_3$. Nonetheless, the atmospheric relevance of the mechanism remains to be investigated.

METHODS

A nitrate ion-based chemical ionization atmospheric pressure interface (CI-APi-TOF) (Jokinen et al., 2012) was applied in Mace Head field campaign to detect HIO$_3$ (Sipilä et al., 2016). We investigated this compound in other locations, such as a boreal forest (SMEAR II station, Hyytiälä) and Antarctica. Laboratory experiment was also performed to produce HIO$_3$ in a well-controlled flowtube. In addition, an iodide ion-based chemical ionization method was applied to extend our capability to detect more iodine-containing gas phase compounds, as shown in the table 1 in their ion forms.

<table>
<thead>
<tr>
<th>Formula</th>
<th>IOI$^-$</th>
<th>OIOI$^-$</th>
<th>HOII$^-$</th>
<th>INO2I$^-$</th>
<th>INO3I$^-$</th>
<th>II$^-$</th>
</tr>
</thead>
</table>

Table 1. Ions detected by Iodide ion-based CI-APi-TOF.

CONCLUSIONS

Diurnal patterns of HIO$_3$ over Antarctica, Hyytiälä forest station and Mace Head are plotted in Figure 1; each line is averaged from one month’s data as shown by the legend. Due to the variation of the photochemistry, the HIO$_3$ in Mace Head and Hyytiälä shows clear diurnal pattern, though the peaking hours are different. On the other hand, the Antarctica data show no diurnal pattern which can be explained by the relatively constant photochemistry during the polar days.
The laboratory experiments suggested that OIO reacts more efficiently with OH to form HIO$_3$ for two reasons. First, Figure 2 shows that HIO$_3$ counts decrease when we introduce CO into the system, which is simultaneously an OH scavenger and an HO$_2$ enhancer.

The second reason comes from the correlation between IOI- and IO$_3$- when we vary photolysed synthetic air flow, which is used to produce Ozone in the system, the concentrations of IO, OIO and OH simultaneously are changed by following reactions R3 to R5.

\[ \text{I} + \text{O}_3 \rightarrow \text{IO} + \text{O}_2 \]  \hspace{1cm} (R3)

\[ \text{H}_2\text{O} + \text{O}_3 \rightarrow 2\text{OH} + \text{O}_2 \]  \hspace{1cm} (R4)

\[ \text{IO} + \text{IO} \rightarrow \text{OIO} + \text{I} \]  \hspace{1cm} (R5)
If reaction R1 is the major production pathway of HIO$_3$, IOI$^-$ should show linear correlation with IO$_3^-$, which is not true as shown by Figure 3. This non-linear correlation implies the reaction R2 might be more efficient in producing HIO$_3$.

Figure 3. IOI$^-$ counts versus IO$_3^-$ counts. IOI$^-$ counts are normalized by I$^-$ counts; IO$_3^-$ counts are normalized by NO$_3^-$ counts.

Further research efforts required to resolve the complete kinetics of HIO$_3$ formation from molecular iodine emissions before the atmospheric relevance of the mechanism can be assessed.

ACKNOWLEDGEMENTS

This work is supported by Finnish Academy (Projects: 296628, 306853, and Centre of Excellence project: 1118615).

REFERENCES


ROLE OF AEROSOL SEED ACIDITY AND NOx IN SOA FORMATION FROM ALPHA-PINENE OZONOLYSIS

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Keywords: AEROSOL MASS SPECTROMETER (AMS), SECONDARY ORGANIC AEROSOL (SOA), HETEROGENEOUS CHEMISTRY, ORGANONITRATES, AEROSOL ACIDITY

INTRODUCTION

Secondary organic aerosol (SOA), formed via gas to particle transition in the atmosphere, accounts for a significant fraction of the tropospheric organic aerosol (Hallquist et al., 2009). SOA plays an important role in cloud formation, visibility and health (Boucher et al., 2013; Hyslop, 2009; Pope and Dockery, 2006). Recently, significant progress has been made in investigating the key precursors that contribute to SOA formation (i.e. Ehn et al., 2014), but still detailed formation mechanisms are unknown for many systems.

The reactive uptake of gas phase constituents could be a very important player in SOA formation (i.e. Surratt et al., 2010). Heterogeneous aerosol chemistry has mainly been focused on isoprene chemistry due to the large abundance of isoprene in the atmosphere. However, previous studies have pointed out that terpenes, such as α-pinene, play a more important role in SOA formation than isoprene (Hallquist et al., 2009). In this study we investigate the role of aerosol seed acidity in SOA formation from α-pinene ozonolysis products under varying amounts of NOx.

METHODS

The measurements were conducted in a 2 m² Teflon chamber under room temperature (26 ± 2°C) and relative humidity around 30 % during June 2016. A constant flow of α-pinene (10 ppb), O₃ (30 ppb), NOx (1 – 10 ppb) and 80 nm ammonium sulfate (AS) or ammonium bisulfate (ABS) seed aerosol was injected to the chamber, resulting in a steady state condition with a residence time of approximately 40 minutes.

The chemical composition of SOA was measured with a High Resolution Long Time of Flight Aerosol Mass Spectrometer (HR-L-ToF-AMS; similar instrument described by DeCarlo et al., 2006). This was, to our knowledge, the first chamber measurements conducted with this AMS type. The HR-L-ToF AMS was sampling through a Teflon inlet with an approximately 1.1 l min⁻¹ flow. The particle losses in the sampling line were assumed to be small due to the losses of charged particles already in the chamber. The sample was hereafter guided through a critical orifice, aerodynamic lens and a chopper (a plate that can be used for blocking the aerosol beam) region to a vaporizer. The vaporizer was heated to approximately 570 C that caused flash vaporizing of the aerosol particles. The vaporized molecules were afterwards ionized with 70 eV electron impact ionization (EI) technique so that they were detectable at the detector after travelling through a long time of flight chamber (L-ToF chamber).

The data used in this study is a difference in signal of the measurements in both chopper closed and open positions. The signal was measured in both positions for 30 minutes. The raw data was processed with Squirrel ToF-AMS Analysis Toolkit v. 1.571 and Pika ToF-AMS HR Analysis v. 1.161.

In this study, four chamber conditions were examined with the HR-L-ToF-AMS. The concentrations of α-pinene (10 ppb) and ozone (30 ppb) were kept constant, as it was described in methods. The conditions are presented below in Table 1.
Table 1. The four experimental steady state conditions investigated in this study. AS refers to ammonium sulfate and ABS to ammonium bisulfate.

<table>
<thead>
<tr>
<th></th>
<th>1st condition</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NOₓ] (ppb)</td>
<td>1 (low)</td>
<td>10 (high)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Seed</td>
<td>AS</td>
<td>AS</td>
<td>ABS</td>
<td>ABS</td>
</tr>
<tr>
<td>[α-pinene] (ppb)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>[O₃] (ppb)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

RESULTS AND CONCLUSIONS

The AMS analysis software divides the detected ions into “families”, depending on the element found in each ion. For example, the “CH family” contains all ions with composition CₓHᵧ₊ and the “CHO₁ family” ions of the form CₓHᵧO₁₊. Figure 1 shows the state of CH, CHO₁, CHO, CHN, and NO families during each steady state condition shown in Table 1. The raw signal (Hz) of each family is normalized by dividing the signal with the SO family raw signal (approximately the mass concentration of the seed).

The CH family signal seems to be quite steady during each condition indicating its independency of aerosol seed acidity or amount of NOₓ. The signal of CHO₁ and CHO families seems to slightly favour the low NOₓ condition, but show no clear difference as a function of acidity. The NO family seems to be fairly constant at each condition. The CHN family (purple trace in Figure 1) seems to have highest, yet complex, dependence on both acidity and NOₓ concentration: the amount of these compounds increases with acidity, as well as with [NOₓ] if the seed is acidic.

This could be explained as follows: The increased NOₓ concentration enhances organonitrate formation in the gaseous phase from alpha-pinene ozonolysis. The uptake of these organonitrates is more efficient at higher acidity due to the availability of H+ to act as a catalyst forming compounds that will not evaporate back to the gaseous phase.

It is somewhat surprising that we measured the CHN fragments from these compounds rather than the CHNO fragments, and more detailed analysis is required to fully understand this process. Especially the oxygen-containing organonitrates will be investigated and data from FIGAERO-measurements (a filter inlet for gases and aerosols; Lopez-Hilfiker et al., 2014) conducted with an I-HR-L-ToF-CIMS (Iodide-adduct High Resolution Long Time of Flight Chemical Ionization Mass Spectrometer; Lee et al., 2014) will be added to the analysis.

ACKNOWLEDGEMENTS

This study was supported by the Academy of Finland (Center of Excellence programme, project number 272041) and the European Research Council (Grant 638703-COALA).
Figure 1. The state of CH, CHO, CHO, CHN, and NO families during each steady state condition shown in Table 1 (1 – 4). The raw signal (Hz) of each family is normalized by the SO family raw signal that originates from the seed aerosol.

REFERENCES


WATER CLARITY AND ATMOSPHERIC FORCING AND THEIR IMPACTS TO GREENHOUSE GAS EMISSIONS FROM LAKES

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Keywords: LAKES, CARBON DIOXIDE, WIND, HEAT, FLUX, THERMOCLINE.

INTRODUCTION

Lakes as net heterotrophic systems have an opposite role than oceans in global carbon balance. Even though lakes cover only 2% of the world’s land surface, it has been estimated that lakes release about 10% of the carbon fixed annually by the terrestrial ecosystems back to the atmosphere (Lehner & Döll, 2004; Le Quéré et al., 2009; Raymond et al., 2013). Turbulence in the water column, especially close to the surface is of crucial importance for gas exchange, and the bottle neck in aquatic gas transfer is in the water (Jähne and Haußecker, 1998). Therefore, correct parameterization of the relationship between surface turbulence and atmospheric forcing is of crucial importance when global estimates of GHG efflux from lakes are derived. Water clarity, on the other hand, affect the thermal stratification of a lake, which in turn affects lake-atmosphere heat exchange and further gas transfer (Heiskanen et al., 2015).

METHODS

The aim of our study was to assess the current global CO₂ evasion estimates from lakes to the atmosphere by comparing parameterizations for k and the significance of wind and heat flux to the gas transfer in small lakes. The unique full ecosystem scale measurement platform called Lake-SMEAR which is connected to SMEARII station at the Hyytiälä Forestry Field Station of Helsinki University was used for conducting the field studies. The measurements include direct flux measurements (eddy covariance) of carbon dioxide, water vapour and methane, continuous profiling of water column carbon dioxide concentration and temperature measurements throughout the water column with a thermistor chain. To improve future predictions of gas evasion from lakes, we focused on the changes in water clarity and how they affect water column physics and processes in the air-water interface. We studied a small boreal lake and used the eddy covariance (EC) method for the high precision data needed, and therefore also aimed to improve the EC methodology on lakes.

CONCLUSIONS

The air-water gas transfer was related to both wind and heat loss during times of seasonal stratification, but only to wind during autumn overturn (Heiskanen et al., 2014). When wind-induced thermocline tilting and resulting spatial variability in surface water CO₂ concentrations was accounted for, average k derived from the measurements dropped from 6.0 cm h⁻¹ to 5.2 cm h⁻¹. This was still over twice the estimate (2.2 cm h⁻¹) calculated with a widely used model for k in lakes suggesting that the global estimates of gas evasion from lakes might be underestimations.

Water clarity was a significant parameter defining the thermal stratification of the lake: a change from clear to dark water would lead to shorter stratification period and lower water column temperatures in small lakes and therefore have significant impact on the lake-atmosphere exchange processes (Heiskanen et al., 2015).
ACKNOWLEDGEMENTS

This study was funded through the Academy of Finland Center of Excellence program (project 272041), Academy of Finland ICOS project (263149), EU ICOS project (211574), Research Foundation of the University of Helsinki, EU GHG-Europe project (244122), EU-project GHG-LAKE, DEFROST (Nordforsk) project, Academy of Finland (project 218094), and University of Helsinki research funds through the project Vesihuusi.

REFERENCES


INTRODUCTION

Freshly formed secondary aerosol particles are small, about one nanometer in size. In favorable conditions these particles can grow to atmospherically relevant sizes and, therefore, it is important to understand the mechanism related to the early phase of growth. Despite of the development of gas and particle composition measurement methods during recent years, the processes and compounds affecting the growth of freshly formed particles are still inadequately known.

In this study we used particle growth model MABNAG to model the growth of nanosized particles during new particle formation events (NPF) at Hyytiälä in 2014. The growth was modelled based on measured gas phase concentrations of organic vapors and model simulations were compared to measured particle number size distributions.

METHODS

MABNAG (Model for Acid-Base chemistry in NAnoparticle Growth) is a monodisperse particle population growth model that combines dynamic condensation calculations to acid-base chemistry that take place inside the particle (Yli-Juuti et al., 2013). The mass flux between gas and particle phase is determined based on equilibrium vapor concentrations and gas phase vapor concentrations, and the dissociation and protonation is taken into account for acids and bases.

To model the nanoparticle growth in atmosphere, eight compounds were used as an input for the model: water, ammonia, sulfuric acid and five different organic compounds. The instruments used to gather the data on gas phase concentrations were HOxROx-CI-APIToF (Mauldin et al. 2016 (in preparation)) for sulfuric acid in spring 2014, Marga for ammonia (Makkonen et al. 2012) and FIGAERO-HRToF-CIMS (from now on FIGAERO) for organics (Lopez-Hilfiker et al., 2014). In addition the meteorological data (relative humidity, temperature and pressure) were used as input for the model, and simulated growth was compared to particle number size distributions measured with Differential Mobility Particle Sizer (DMPS).

Instead of modelling condensation of each individual organic vapor, the organic compounds measured with FIGAERO were grouped to five model compounds. In one group we included compounds that
were identified as dimers and the rest of the organic compounds were divided into four groups based on their saturation concentration, following the volatility basis set (VBS) approach (Donahue et al., 2006). The saturation vapor concentrations ($C^*$) for the four VBS bins were $10^{-5}$, $10^{-3}$, $10^{-2}$ and $10^{-1}$ µg m$^{-3}$. All compounds with lower $C^*$ than $5 \times 10^{-4}$ µg m$^{-3}$ are included in the lowest bin and the other bins include compounds from range $0.5 \times 10^{-4} < C^* \leq 5 \times 10^{-4}$ µg m$^{-3}$ ($i=3, 2, 1$ respectively). Compounds with higher $C^*$ than $5 \times 10^{-1}$ µg m$^{-3}$ were neglected, for their contribution to the growth is insignificant. Two different methods were used to calculate the saturation vapor concentrations. One is based on the amount of oxygen and carbon atoms in a molecule and was introduced by Donahue et al. (2011), and other was the SIMPOL.1 method (Pankow and Usher, 2008). The SIMPOL.1 is based on structural form of the compounds and since only the atomic composition is obtained from FIGAERO, some assumptions need to be made about the structure; In our model we have assumed that all possible oxygen atoms are forming carboxyl groups and in case of odd number of oxygen atoms, one oxygen was in a carbonyl group, i.e. a ketone. For each organic model compound we assigned properties (saturation vapor pressure, molar mass and diffusion coefficient) based on the concentration weighted averages over compounds included in that group and average over the duration of each NPF-event. In case of missing data during event, the daytime average (from 8am to 6pm) of concentrations over whole measurement period was used. The model simulations were initialized with a particle that contained 40 sulfuric acid molecules and corresponding water and ammonia according to their gas-particle equilibrium constrained by ambient gas phase observations.

RESULTS

The modelled growth of a particle compared to DMPS-measurements for one NPF event can be seen in figure 1a. For this day, 16.4.2014, the model reproduces very nicely the measured particle growth, as was the case in general for spring 2014, although for some NPF events the growth rate was overestimated.

As the particle phase acid-base chemistry is included in MABNAG, we studied the effect of organic salt formation on the particle growth. For this, we performed model runs assuming that all the organics were either weak or strong acids (diacids with dissociation constants $10^{-3}$ and $10^{-5}$ mol$^2$ kg$^{-2}$ for strong acids and $10^{-5}$ and $10^{-10}$ mol$^2$ kg$^{-2}$ for weak acids), or neutral (non-reactive) compounds. The differences between the model simulations performed with these three assumptions were very small, which suggests that the possible dissociation of organic acids was not an important factor in the nanoparticle growth during the studied NPF days. According to the model, the organic compound with the lowest saturation concentration contributed most in the particle growth. This is seen in figures 1b and 1c for the example day. Compared to this one, the contribution of other organics in the particle growth was rather small (combined mass fraction less than 20%), and in some cases their contribution increased somewhat with increasing particle size. Also the contribution of sulfuric acid and ammonia in the nanoparticle growth was much smaller compared to the total contribution from organics.
CONCLUSIONS

The results of the study are promising; the combination of FIGAERO measurements for gas phase concentration of organics and the MABNAG model with VBS approach for calculating the growth of nanoparticles in atmosphere seems to produce the observed nanoparticle growth nicely for spring 2014. However, more studies are needed to confirm the validity of the method. Our results suggest that grouping organic compounds to model compounds using the VBS may be a valid approach when simulating the nanoparticle growth, which is an encouraging results regarding large-scale models where simplifications of the processes are often necessary.

Figure 1. (a): Modelled evolution of particle size (black line) and the measured particle number size distribution on 16.4.2014. (b): Modelled mass fractions of the compounds in particle phase as a function of particle size for the same day. (c): Modelled fraction of dry mass increase rate accounted by the different compounds as a function of particle size.
REFERENCES


FREE AMINO ACIDS IN ATMOSPHERIC AEROSOLS IN BOREAL FOREST

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Keywords: FREE AMINO ACIDS, DNA, BACTERIA, PRIMARY BIOLOGICAL AEROSOL PARTICLES.

INTRODUCTION

Primary biological aerosol particles (PBAPs) are emitted to the atmosphere from vegetation and other living organism. PBAPs include e.g. pollen, fungal spores, bacteria, viruses and cell fragments of plants and animals (Després et al., 2007). Their importance to atmospheric chemistry and physics has increased interest towards their reliable determination. Traditionally, living organisms have been studied in particles with cultivation (highly specific) or by microscopy (light or fluorescence). However, molecular genetic analysis techniques are nowadays most frequently used, since they provide information not only about viable cells, but also on uncultivable or dead cells or on plant or animal fragments. Another approach to determine particles of biological origin is based on chemical tracer techniques. The clear advantage of chemical tracers, that are not limited only to amino acids, carbohydrates, proteins and peptides, and rarely lipids, is the possibility for quantitative analysis, while the main disadvantage is disability to identify different biological species.

PBAPs are considered to be a major source of proteinaceous materials in the atmosphere (Matos et al., 2016). It is suggested that proteins have undergone enzymatic hydrolysis or thermal or photochemical decomposition into peptides or free amino acids (FAAs). Amino acids can serve as markers for various kinds of PBAPs. The origin of FAAs has not yet been fully identified, although some possible sources, such as biomass burning, volcanic emissions and bubble bursting process in marine environment, have been recognized. FAAs are a potentially important class of hydrosopic compounds for atmospheric chemistry, due to their low vapor pressures and high water solubility. In fact some amino acids have been demonstrated to be effective in cloud condensation and ice-forming nuclei materials.

The aim of this study was to determine the FAAs concentrations in atmospheric aerosol samples collected in boreal forest. Different particle size fractions were collected throughout the year in order to determine the annual variation and to identify possible sources. The samples were analyzed by using hydrophilic interaction liquid chromatography combined with triple quadrupole mass spectrometer operated in multiple reaction monitoring mode. This analytical method allowed the analysis of 20 underivatized amino acids. The obtained FAA data was compared to previous results from Sietiö et al. (2015), where the abundance of bacteria and fungi were characterized and the total DNA concentration in aerosol particles given. The preliminary results from comparison of FAAs with the aforementioned PBAP are presented here with main focus on FAAs.
METHODS

The aerosol samples were collected between February and October 2014 at the SMEAR II station in Hyytiälä, Finland. A Dekati PM10-impactor was used for the sampling of four particle size fractions (<1.0, 1.0-2.5, 2.5-10 and >10 µm). The sampling flow rate was on average 29 L/min and the collection time was from two to four days (sampling volume 76-144 m³). The collection filters were 25 mm polycarbonate membranes (Whatman Nuclepore Track-Etched Membranes) with no holes for the three largest particle size fractions. To prevent particles bouncing away from the collection substrates, membranes were smeared with diluted Apiezon L vacuum grease. The smallest size fraction (<1.0 µm) was collected on a 47 mm teflon filter with 2 µm pore size. After sampling, the filters were dried, placed inside a closed petri dish and stored in -20 °C.

Ultrasonic assisted extraction with 0.1% formic acid as solvent was used for the extraction of free amino acids from the collection substrates. Filter was removed from the petri dish with tweezers and placed into a test tube. Due to the grease used to cover the filters, there was a spot of grease left onto the surface of the petri dish. In order to recover all the particles, the grease spot was dissolved with hexane and the solute was pipetted into the test tube. Filter was spiked with known amount of labelled internal standard mixture solution. The sample was sonicated at room temperature for 15 minutes with 2 mL of 0.1% formic acid. Sonication was repeated twice with 2 mL and 1 mL of 0.1 % formic acid for 10 minutes each time. Finally, 1 mL of toluene was added into the extract solution in order to ensure that the grease will partition into the organic phase. The solution was vortexed and centrifuged. Aqueous layer was separated and filtered through a 0.45 µm filter into a 5 mL volumetric flask. The samples were stored at 4 °C and analyzed within 72 hours.

The analyses were performed with an Agilent 1260 Infinity HPLC coupled to an Agilent 6420 triple quadrupole mass spectrometer (Agilent Technologies, USA). Electrospray ionization in positive mode was used. The column used was a SeQuant ZIC-chILIC (100 x 2.1 mm, particle size 3 µm, 100 Å, Merck KGaA, Germany). The column temperature was maintained at 30 °C and the injection volume was 3 µL. Eluent A was 0.01% acetic acid in acetonitrile and eluent B was 0.01% acetic acid in ultrapure water. The optimized gradient program was as follows: 0-10 min, 20% eluent B; 10-20 min, 60% eluent B; 20-40 min, 60% eluent B; 40-45 min, 20% eluent B and equilibration for 25 min. All the mobile phase gradient changes were linear and the flow rate was 150 µL/min. Mass spectrometer source parameters were optimized and they were set as follows: drying gas temperature 350 ºC, drying gas flow rate 12 L/min, nebulizer pressure 40 psi and capillary voltage +4000 V. The MS was operated in a dynamic multiple reaction monitoring (MRM) mode. Precursor ions and product ions were selected based on observations during method development. Fragmentor voltage, collision energy and cell accelerator voltage were optimized for each amino acid separately.

For analyzing the importance of the sampling time and the aerosol filter size, multivariate analysis of variance (MANOVA) was performed for the gene copy numbers of bacteria, *Pseudomonas* and fungi as well the presence/absence transformed FAAs data. The MANOVA was performed with the adonis-function of the vegan package (Oksanen et al., 2016), and the FAAs and gene copy number data were set as response variables while sampling month and aerosol filter size were set as explanatory variables. In addition, the FAAs data was compared to the gene copy numbers data by means of regression analysis and correlation between each variable was studied. The three largest particle size fractions were included in these data analyses, because the gene copy numbers data was only analyzed from these size fractions.

RESULTS

The concentration of FAAs was highest during late spring and early summer during the pollen season peak, the range being between 0.3 to 2087.8 pmol/m³, when all size fractions were taken into account. In addition, the concentration of FAAs risen again in autumn, when other PBAPs (e.g. fungal spores) emissions reached their maximum concentration (Figure 1). The annual pattern of FAAs concentration was similar to PBAP
annual pattern observed previously in the same sampling site (Manninen et al., 2014). Furthermore, similar annual pattern was observed between FAAs and extracted DNA concentration. The amount of extracted DNA was also highest during early summer and autumn (see Sietiö et al. (2015)).

Figure 1. Total concentration of free amino acids in aerosol samples.

The relative concentration of FAAs had different seasonal variation in different particle size fractions (Figure 2). The relative FAA concentration was highest in the <1 µm fraction during late winter, whereas during the pollen season, amino acids were mainly in the >10 µm fraction. Seemingly during summer months FAAs are more evenly distributed in all size fractions. In autumn FAAs are mainly present in the <10 µm particles.

Figure 2. Amino acid particle size distribution in aerosol samples.
In the size distribution some clear tendencies were observed, such as high glycine level in the <1 μm fraction and higher glutamine and glutamic acid levels in the <10 μm fractions (Figure 3). Glycine was the most dominant amino acid in the particles <1 μm, whereas in the other size fractions amino acids were more evenly distributed. Figure 3 was plotted without the pollen season samples to get more representative distribution. With the pollen season samples that were dominated mainly by proline and arginine and present in huge concentrations, the distribution would have been distorted.

![Pie charts showing amino acid distribution in different size fractions.](image)

Figure 3. Amino acid relative concentration distribution in each size fraction. Samples from pollen season are excluded.

The results from the MANOVA analysis indicated that seasonal variation explained the observed variation across the whole amino acid and gene copy number data with statistical significance (p<0.001). In addition, the size of the aerosol filter was statistically significant factor for explaining the observed variation (p<0.05). The preliminary results from regression analysis revealed that the concentration of FAAs correlates with the amount of bacteria found in each size fraction: 1-2.5 μm (R^2=0.93, p<0.001), 2.5-10 μm (R^2=0.86, p<0.001), >10 μm (R^2=0.93, p<0.001) and total particles (R^2=0.97, p<0.001). However, the correlation between FAAs and bacteria is mainly due to the high abundance of both variables during the pollen season. If the pollen season samples are excluded, the correlation would be negligible although in the total particles there was still borderline statistical significance (R^2=0.29, p<0.05). Between FAAs and Pseudomonas or fungi, no statistically significant correlation was observed.

**CONCLUSIONS**

Overall, the total concentrations of FAAs in the aerosol filters had a distinct seasonal variation being the most abundant in late spring and early summer, and during autumn. Furthermore, some trends in the amino acid distributions in different size fractions in aerosol filters were observed. These detected variations agree with our previous studies.
The future work will focus on the clarification of the correlation of individual amino acids with different PBAPs. Amino acid distribution in different particles sizes can provide additional information on their possible sources and further data analysis is required to explain the observed tendencies. In addition, the origin of high bacterial copy numbers during pollen season will require more thorough investigation in order to elucidate the true relationship between abundances of bacteria and FAAs during the pollen season. Furthermore, extra studies are needed to enlighten the relationship between seasonal drifts in FAAs and fungal and bacterial copy numbers. Since according to the profiles of FAAs the abundance of bacteria is highest in late spring and early summer whereas fungi are more abundant in autumn, specific fungal or bacterial marker-FAAs would be beneficial in further studies.

ACKNOWLEDGEMENTS

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REFERENCES

MEASUREMENTS OF VOLATILE MONOCARBOXYLIC ACIDS IN THE AIR OF A BOREAL FOREST

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INTRODUCTION

Organic acids comprise about a quarter of the non-methane hydrocarbons in the atmosphere (Khare et al., 1999). They are known to have both anthropogenic and biogenic sources (Mellouki et al., 2015). In addition, they are produced in ambient atmospheric air from the oxidation of other volatile organic compounds (VOCs) (Orzechowska et al., 2005).

The volatile organic acids (VOAs) react with hydroxyl radicals in the air or undergo dry or wet deposition. Aqueous phase reactions provide a sink for water soluble VOAs, but reactions of other VOCs in aqueous phase may also be a source of VOAs (Ervens et al., 2013). The VOAs potentially play a significant role in the production of secondary organic aerosols (Carlton et al., 2006). Acids act as an organic coating of aerosol particles (Russell et al., 2002) and they also undergo heterogeneous reactions on particles (Shen et al., 2013). However, VOAs are expected to occur mainly in the gas phase (Yatavelli et al., 2014).

Due to the lack of sensitive enough measurement methods for detecting VOA concentrations in ambient air, the knowledge of VOAs other than formic and acetic acid is limited. In the present study we developed an in situ GC-MS measurement method for measuring monocarboxylic VOAs with two to seven carbon atoms (C2-C7) with two hour time resolution at ambient air concentration levels, which were used to measure ambient air concentrations in a boreal forest site.

METHODS

A method for measurements of VOAs in air was developed for an in-situ thermal desorption unit (Unity 2 + Air Server 2, Markes International Ltd.) with a gas chromatograph (Agilent 7890) and a mass spectrometer (Agilent 5975C). Samples were taken every other hour. The sampling time was 60 min and the flow 30 ml min⁻¹. In the 3 m long fluorinated ethylene propylene (FEP) inlet (1/8 inch I.D.) an additional by-pass flow of 2.2 l min⁻¹ was used to avoid losses of the compounds on the walls of the inlet tube. Samples were collected directly into the cold trap (U-T17O3P-2S, Markes International Ltd.) of the thermal desorption unit. All lines and valves in the thermal desorption unit were kept at 200°C. Water was removed by keeping the hydrophobic cold trap at 25°C during sampling and using a post sampling line purge (10 minutes, 30 ml min⁻¹), post sampling trap purge (10 minutes, 20 ml min⁻¹) and pre-trap fire purge (10 minutes, 10-11 ml min⁻¹). For desorption the cold trap was heated to 300°C for 3 minutes and flushed with a helium flow of 10-11 ml min⁻¹. The polyethylene glycol column used for separation was the 30-m-long DB-WAXetr (J&W 122-7332, Agilent) with an inner diameter of 0.25 mm and a film thickness of 0.25 µm. Helium (99.99996%) was used as a carrier gas. During the analysis the GC oven was first kept at 50°C for 10 min, heated to 150°C with the rate of 4°C min⁻¹ and then to 250°C with the rate of 8°C min⁻¹, where it was kept for 5 min. The total run time was 52.5 min.

The system was calibrated using liquid standards in Milli-Q water injected into adsorbent tubes filled with Tenax TA and Carbopack B. After injection the tubes were flushed with a nitrogen (N2, 99.9999%) flow of 80 ml/min for 10 minutes to remove the water. Standard tubes were desorbed and analysed using the same method as for the samples. Fresh standards were prepared from a volatile free acid mixture (CRM46975,
Supelco) one day before the analysis. The stability of the mass spectrometer was followed by running gaseous field standards containing aldehydes and aromatic hydrocarbons after every 50th sample taken and using tetrachloromethane as an internal standard. The concentration of tetrachloromethane in ambient air is stable, thus it was possible to detect sampling errors or shifts in calibration levels by following its concentration.

An ambient air sampling campaign was conducted at SMEAR II forest research station in Hyvinkää (61°51'N, 24°17'E, 181 m a.s.l.), Finland, between 11 and 27 June 2015. During the measurement campaign at SMEAR II a PTR-TOFMS (Ionicon Analytik GmbH; Jordan et al., 2009) was run in parallel with in situ GC-MS.

The PTR-TOFMS instrument was operated at a drift tube pressure of 2.3 mbar and a drift tube voltage of 600V. These settings resulted in an $E/N$ of 130 Td, where $E$ is the electrical field strength and $N$ the gas number density. The air was sampled at a flow of 20 l min$^{-1}$ through a 3.5 m PTFE inlet, which had an inner diameter of 4 mm. A total flow at the rate of 500 ml min$^{-1}$ went to the instrument via a three way valve (type: 6606 with ETFE, Bürkert GmbH & Co. KG), 10 cm of 1.6 mm (I.D.) PTFE and 10 cm of 1 mm (I.D.) PEEK tubing. There, 30 ml min$^{-1}$ of the flow was sampled and the remainder served only as a by-pass flow in order to decrease the response time and wall losses. A 20 min background measurement was performed three times a day, during which the air from the 3.5 m inlet was let through a custom build catalytic converter. The second port of the three way valve was used for this. The calibration gas did not contain acetic acid or propanoic acid, and their fragmentation pattern was not quantified. Their sensitivity was estimated as being 50% of the acetone sensitivity. The instrumental background for acetic acid was clearly correlated with ambient measurements. This can be explained by a memory effect (of the inlet and/or instrument) of those compounds. Therefore, the reported concentrations of acetic acid are underestimated, as an excessively high background signal had been subtracted. The mean detection limits for acetic and propanoic acids during the campaign were 34 and 8 pptv, respectively.

### RESULTS

The method was validated in the laboratory and tested on the ambient air of a boreal forest in June 2015. Experimentally determined recoveries of VOAs from FEP and heated stainless steel inlets were acceptable and different VOAs were fully desorbed from the cold trap and were well separated in the chromatograms. Detection limits varied between 1 and 130 pptv and total uncertainty of the method at mean ambient mixing ratios ranged between 16-76% (Table 1).

All straight chain VOAs except heptanoic acid in the ambient air measurement at SMEAR II were found with mixing ratios above the detection limits. The highest mixing ratios were measured for acetic acid (Figure 1). The mixing ratios of isobutyric, isoheptanoic and heptanoic acids stayed below their detection limits during the whole campaign. The mixing ratios generally decreased with increasing carbon number except for hexanoic acid. Hexanoic acid was more abundant than pentanoic acid. Such a VOA profile was also seen in the measurements of Kawamura et al. (2000) but in the urban air of southern California in 1984.

<table>
<thead>
<tr>
<th></th>
<th>RT (min)</th>
<th>BL (pptv)</th>
<th>DL (pptv)</th>
<th>$U_{\text{prec}}$ (%)</th>
<th>$U_{\text{tot}}$ (%)</th>
<th>Mean (pptv)</th>
<th>Min (pptv)</th>
<th>Max (pptv)</th>
</tr>
</thead>
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<td>130</td>
<td>7</td>
<td>16*</td>
<td>1160</td>
<td>910</td>
<td>1520</td>
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<tr>
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<td>5</td>
<td>23</td>
<td>15</td>
<td>32</td>
<td>81</td>
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<tr>
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<td>-</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>20</td>
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<tr>
<td>Butanoic acid</td>
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<td>7</td>
<td>19</td>
<td>39</td>
<td>40</td>
<td>20</td>
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</tbody>
</table>
Isopentanoic acid 38.3 - 1 - - 1 <DL 4
Pentanoic acid 40.0 - 5 38 76 10 <DL 20
Isohexanoic acid 41.6 - 13 - - <DL <DL <DL
Hexanoic acid 42.5 - 7 20 40 20 <DL 80
Heptanoic acid 44.7 - 19 - - <DL <DL <DL
Benzene 8.4 6 20 53 108 20 <DL 90
Toluene 12.4 8 9 35 72 20 <DL 70

*Acetic acid has an additional error source which was not taken into account in these calculations

Table 1. Retention times (RT), blank values (BL), detection limits (DL), precision (U \text{Prec}) and total expanded uncertainties (U \text{tot}) together with mean (Mean), minimum (Min) and maximum (Max) mixing ratios for studied compounds during the measurement campaign at SMEAR II in June 2015. Precision and uncertainties were calculated for mean ambient air mixing ratios.

Hexanoic acid had the highest relative variations in mixing ratios (Figure 1). The variation in sources and source strengths together with higher reactivity of hexanoic acid may explain this. Reaction rates of VOAs with hydroxyl radicals increased with increasing carbon number (Mellouki et al., 2015) and trees and other vegetation are known to produce stress induced emissions of green leaf volatile organic compounds which are aldehydes, esters and alcohols with six carbon atoms (Scala et al., 2013). Oxidation of these compounds...
could be a source of hexanoic acid. However, based on the current knowledge even direct emissions of hexanoic acid cannot be ruled out.

Butanoic acid emissions peaked (100 pptv) on 14 June (Fig. 1). This peak occurred at the same time as the peak of 1-butanol (2500 pptv, not shown). 1-Butanol was being used at the same site in other instruments including particle counters. During malfunctions of these instruments 1-butanol may have been released into the ambient air. Butanoic acid was expected to be produced in the oxidation reactions of 1-butanol in the atmosphere. Maximum mixing ratio peaked in the middle of the night (1:30-2:30 AM, local time), which gave an indication that butanoic acid has been produced from nitrate radical reactions.

Figure 2. Mean diurnal variation of the mixing ratios with standard deviations (error bars) at SMEAR II between 11 and 27 June 2015.

Acetic and propanoic acids had the highest mixing ratios during the day and lowest during the night (Fig. 2). Hexanoic acid had the opposite diurnal variation with the maximum concentration occurring during the night. Butanoic and pentanoic acids did not show any clear diurnal cycle. Direct emissions from vegetation and production in photochemical reactions are expected to be highest during the day when there is more light and higher temperature. However, degradation of VOAs and boundary layer mixing are also faster during the day and this phenomenon, in addition to the lower boundary layer present during the night, may explain the high night-time concentrations of faster reacting VOAs. High night-time concentrations have also been measured at the site for monoterpenes even though their emissions are clearly highest during the day (Hakola et al. 2012). During the night VOAs may also be produced from ozone and nitrate radical reactions.
The PTR-TOFMS measured acetic and propanoic acids, whereas the other VOAs remained below their respective detection limits for that instrument. The variations of the mixing ratios were quite similar for both instruments (Fig. 3). The correlation was relatively good when the mixing ratios of acetic acid (GC > 1300 ppt, $R^2=0.78$) and propanoic acid (GC > 80 ppt, $R^2=0.52$) were highest. Low correlations with lower values were expected due to the high uncertainties for both instruments when the levels of the VOAs being analysed were close to their respective detection limits.

The mean mixing ratios of acetic and propanoic acids measured by GC-MS were 5.7 and 2.3 higher than those measured by the PTR-TOFMS method. The main reason for the large discrepancy for acetic acid is the overestimation of the background due to memory effects in the PTR-TOFMS as discussed in Method section. The measurements were conducted in separate containers, but were close to each other (5m). Therefore, only small differences were expected, not such large factors. The overall variations of the signal of the two instruments are comparable, thus the main difference between them seems to be due to the background problem or problems in calibrations of the instruments. The calibration curve of acetic acid for the GC-MS measurements suffered from high background at low levels. More accurate measurements of these compounds require that better calibration methods are developed. In addition to this, using different inlet line and valve materials could help to reduce the memory effect and lower the background.

![Figure 3](image)

**CONCLUSIONS**

A novel in situ GC-MS method for the quantification of volatile organic acids was evaluated. Despite the relatively high uncertainty, the method is uniquely capable of detecting VOAs at low concentrations with only a 2-hour time resolution. Detection limits varied between 1 and 130 pptv between individual VOAs. The system performed well for ambient air measurements at a boreal forest site. We found that acetic acid had the highest mixing ratios, but hexanoic acid concentrations varied the most. The lightest VOAs (acetic and propanoic acids) had their maxima in the afternoon, whereas hexanoic acid had an opposite diurnal variation.

The mixing ratios of acetic and propanoic acids measured with the novel GC-MS method were compared to PTR-TOFMS data. Similar variations of mixing ratios were captured by both analytical set-ups, but absolute levels deviated significantly. High background concentration was a problem for both instruments.
and especially for the measurement of acetic acid by the PTR-TOFMS. Replacing the inlet line and valve materials could improve the situation. A better calibration method especially for acetic acid, in GC-MS measurements, would also improve the quality of the data for acetic acid.

Nevertheless, this novel in situ GC-MS method will allow us to study diurnal and seasonal variations of VOAs in ambient air. These new datasets will benefit atmospheric chemistry and new particle formation studies.

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INTRODUCTION

Clouds and aerosol particles play an important role in climate, air quality and weather (IPCC, 2013). Despite intensive research efforts, the scientific understanding on the interaction between aerosol particles and clouds remains limited. Advanced numerical models can be used to assess interactions between air quality and climate change, but, in order for any model to provide reliable results, observations and process-level understanding on clouds, aerosol, precipitation, and boundary layer dynamical evolution are critical for model initialization and evaluation (Barthlott and Hoose, 2015; Heinze et al., 2016). The World Meteorological Organization (WMO, 2014) reports that the major weaknesses of current weather forecasting are related to lacking or inadequate observations, amongst the other basic observations, on clouds, precipitation and hydrological cycle. This holds also for climate modelling. However, deployment of ground-based remote-sensing atmospheric observations in Finland and elsewhere in the Scandinavian area, a region highly vulnerable to climate change and pollution, is still largely missing from the current European climate modelling projects. Therefore, the Finnish Meteorological Institute (FMI) has invested heavily in enlarging the remote-sensing measurement capacity of clouds, aerosol particles and boundary layer during the past five years (Hirsikko et al., 2014; Vakkari et al., 2015). One of the main research aims of the FMI ground-based remote-sensing infrastructure include cloud properties and their evolution, together with their coupling with the environment over the arctic, continental and marine Finland. Here, insights into the recent cloud research of the working group are introduced.

METHODS

The new ground-based remote-sensing infrastructure of FMI has been described by Hirsikko et al. (2014) and Table 1 summarizes deployment of the FMI cloud radar together with supplementing remote-sensing and in-situ sensors. In 2014, Hyytiälä, measurement station of the University of Helsinki, hosted the Biogenic Aerosols – Effects on Clouds and Climate (BAECC) measurement campaign by the American Mobile Facility (AMF; Petäjä et al., 2016). Every autumn Pallas hosts an extensive cloud experiment (PaCE; Anttila et al., 2012) and in autumn 2015, ground-based remote-sensors participated in the autumn cloud experiment for the first time.

Investigation of cloud macro and micro physical properties is based on the Cloudnet scheme (Illingworth et al., 2007), a standardized processing methodology applied routinely to ground-based remote-sensing of cloud at European supersites within the European project ACTRIS (Aerosol, Clouds and Trace gases InfraStructure network). Here, we exploited the cloud hydrometeor classification provided by Cloudnet (Figure 1). Synergetic observations of cloud radar and ceilometer/lidar enable the classification of targets into different hydrometeor groups (i.e. rain, liquid and ice/mixed phase clouds). The classification allows...
more than one hydrometeor class to exist in the same volume, but the standard scheme is often limited to
detecting only the most prominent hydrometeor class. It is known that mixed-phase clouds containing both
ice and super-cooled liquid are common but that the super-cooled liquid layer is not always easy to detect.
To improve detection, a new technique based on cloud radar Doppler velocity profile data and subsequently
calculated dissipation of turbulent kinetic energy was used.

RESULTS

Investigation of cloud hydrometeor classification based on the Cloudnet target classification clarified that
super-cooled liquid water is frequently observed throughout the year in clouds occurring over Finland
(Figure 1). These layers can persist for several hours, whether precipitating or not. Super-cooled liquid water
layers have a large radiative impact, together with direct and indirect influences on other atmospheric
properties, precipitation, and can initiate contact freezing. However current numerical weather prediction
models find super-cooled liquid water layers a challenge to forecast.

A close investigation of cloud radar Doppler velocity and spectral width profiles, showed that the standard
Cloudnet scheme very likely fails to identify a significant fraction of super-cooled liquid water layers. This
is due to the fact that liquid water detection is based on ceilometer or lidar profiles; a lidar signal is severely
attenuated by liquid water clouds, and thus, potential multiple liquid water layers above the first layer will
necessarily remain unidentified. The standard parameter from a cloud radar, reflectivity factor, is
proportional to droplet size to power 6 which means that a few large particles (ice, snow) will exhibit much
larger reflectivity than a large number of small water droplets; in fact the reflectivity from liquid water layers
may be below the detection limit of the cloud radar. Therefore, we investigated the possibility of identifying
super-cooled liquid water layers based on their turbulent signature (liquid layers are typically much more
turbulent than ice clouds) using cloud radar Doppler velocity profile data. Figure 2 shows an example day
where a super-cooled liquid water layer persists at the top of the precipitating ice layer throughout the day
(between 1.30 AM and 24 PM). Additionally, from 6-9 AM, as many as three distinct layers in the velocity
parameters can be identified simultaneously within a profile, attributed to three separate super-cooled liquid
water layers existing simultaneously. The standard ceilometer–based detection is often able to diagnose one
super-cooled liquid layer (green colour in Figure 1) but the ceilometer signal can be attenuated by
precipitating snow before even detecting the first layer.

The examples shown in Figures 1-2 reflects the benefit of including Doppler velocity information to identify
multiple super-cooled liquid water layers, and a new method was developed and tested against coincident
lidar depolarization observations, when possible. The new method shows improved performance over the
standard method although it does not identify all super-cooled liquid water layers nor their full depth. In
conclusion, multi-sensor synergetic retrievals, supplemented with new developments in data analysis, show
the best performance.
Figure 1. The Cloudnet target classification of hydrometeors at Kuopio on 22.11.2014.

Figure 2. Cloud radar reflectivity factor, Doppler velocity and spectral width at Kuopio on 22.11.2014.
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ORGANIC AEROSOL VOLATILITY DISTRIBUTION IN A BOREAL FOREST USING TWO INDEPENDENT METHODS

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Keywords: VOLATILITY, TDMA, PMF, VAPORIZATION ENTHALPY.

INTRODUCTION

Atmospheric aerosols influence Earth’s climate both directly and indirectly through affecting the radiation balance, altering the albedo, lifetime and precipitation patterns of clouds (IPCC 2013). However, uncertainty in the spatial and temporal variability of the aerosol size distribution, chemical composition and physicochemical properties make it difficult to quantify the aerosol climate effects. In terms of aerosol chemical composition, the biggest challenges are due to the presence of a vast number of different organic components in aerosol particles, the physical-chemical properties of which vary largely in the atmosphere (e.g. Jimenez et al., 2009). One of the key physicochemical properties of atmospheric organic compounds is their volatility, which determines their partitioning between the gas and particle phase (Bilde et al., 2015).

Different compounds evaporate differently at different temperatures depending on their volatilities. Hence, measuring the evaporation of particles upon heating provides direct information on their volatilities. A Tandem Differential Mobility Analyzer (TDMA) coupled with thermodenuders (TD) where particle are heated, shortly called volatility-TDMA (VTDM), are often used to obtain volatility information on particles. More quantitative information on the volatility distribution can be further obtained by interpretation of the measurement data with a kinetic evaporation model (e.g. Riipinen et al., 2010) that describes the evaporation rate of aerosols inside the TD.

Positive Matrix Factorization (PMF) has been widely used in chemical composition data to allow separating organic aerosol (OA) mass spectra into individual groups based on their bulk chemical characteristics. PMF analysis can provide information on the OA sources and atmospheric processing (Lanz et al., 2007; Huffman et al., 2009; Zhang et al., 2011). Even though there have been multiple studies using PMF to identify different organic OA groups from ambient data (Ulbrich et al., 2009; Ng et al., 2010), especially the semi-volatile oxygenated organic aerosol (SV-OOA) and low-volatility oxygenated organic aerosol (LV-OOA) groups, to our knowledge there are only few studies (Cappa and Jimenez, 2010; Paciga et al., 2016) attempting to connect the oxygenation levels from these two OOA groups with the
volatility of OA obtained from the TD data. Comparing the volatility distribution obtained using a mass transfer model and VTDMA data to the oxidation level derived from the AMS data using PMF can help in quantifying the volatilities of SV-OOA and LV-OOA.

METHODS

The measurements were performed at the Hyytiälä SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations II) between 14 April and 31 May 2014. In this study, the evaporation behavior of submicron aerosols was investigated using a Volatility Tandem Differential Mobility Analyzer (VTDMA), which is part of a Volatility-Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA) system (Hong et al., 2014). A High-Resolution Aerosol Mass Spectrometer (HR-AMS, Aerodyne Research Inc., Billerica, USA) was used to determine the chemical composition of aerosol particles during the experimental period. A Sunset semi-continuous OC/EC analyzer was deployed to determine the mass concentrations of organic carbon (OC) and elemental carbon (EC) concentrations in aerosols using a thermal-optical protocol (Bauer et al., 2009).

A time-dependent evaporation model (Riipinen et al., 2010) was used to simulate the evaporation of aerosols for a monodisperse aerosol population in a heated flow tube by solving the mass transfer equations. The volatility of the aerosol constituents was described by the effective saturation concentration, \( C^* \), at 298 K. For the model input, the ambient particles were assumed to be a mixture of six species, including three organic species with different volatilities having distinct \( C^* \) values (ELVOA, LVOA and SVOA) plus three inorganic components ammonium nitrate (AN), ammonium sulfate (AS) and elemental carbon (EC). AN and AS were assigned with their own characteristic effective saturation vapor concentration and effective vaporization enthalpies obtained from laboratory measurements. Elemental carbon (EC) was assumed to be non-volatile. As a result, the corresponding average volatility distribution of the ambient aerosol was obtained by letting the difference between the measured and modelled evaporation of the ambient aerosol to reach a minimum with a certain pair of mass fractions of these three organic groups together with known mass fractions of AS, AN and EC from HR-AMS and OC/EC measurements.

In this study, PMF analysis was applied by using the PMF2 algorithm implemented with the user-interface Sofi by Canonaco et al. (2013) to the organic aerosol data measured by the HR-AMS. Two organic aerosol groups (SVOA and LVOA) with different volatilities were separated from the AMS data using the PMF method. The factor separation was based on the oxygenation levels of organics, specifically the relative abundance of mass ions at \( m/z \) 43 (f43) and \( m/z \) 44 (f44) (e.g. Aiken et al., 2008).

RESULTS AND DISCUSSION

In Fig. 1, we compare the modelled organic mass fractions of different volatilities (different \( \Delta H_{\text{VAP}} \) values for organics) against the ones obtained from PMF analysis. The dashed lines are the 1:1 lines, while the solid lines show linear least-squares fit to the data points. The correlation coefficients for the comparisons are relatively similar for the models results using \( \Delta H_{\text{VAP}} \) as 60 kJ/mol (see Fig. 1a and b; \( R=0.48 \)) compared to the one using \( \Delta H_{\text{VAP}} \) as 80 KJ/mol (see Fig. 1c and d; \( R=0.41 \)). However, as can be seen from Fig. 1e and f, using \( \Delta H_{\text{VAP}} \) as 100 kJ/mol leads to clearly worse correlation (\( R=0.25 \)). Considering both the correlation coefficient and the 1:1 correspondence of the values, the model results using enthalpy value of 80 kJ/mol for all three organic groups provide the best agreement with the PMF results. On the other hand, Paciga et al. (2016) studied the volatility distribution of the PMF-derived organics and estimated that almost half of the SVOC, which was determined from PMF, is semi-volatile, while 42% is low-volatile and 6% is extremely low-volatile. This suggests that the two PMF-derived organic groups, commonly labeled for their oxidation levels, might not be directly linked to their actual volatilities.

We also investigated the median volatility distribution of organics during the whole campaign using the two methods as shown in Fig. 2. A constant \( \Delta H_{\text{VAP}} \) value of 80 kJ/mol for organics was chosen here for the
model. As seen from Fig. 2, for the current dataset used SVOA contribution to the total organic aerosol mass was 30% PMF results, which is somewhat lower than the SVOA contribution (approximately 40%) obtained by the model. Moreover, the model estimated that the fractions for LVOA and ELVOA of the total OA mass were 34% and 26%, respectively.

Figure 1. Mass fractions of SVOA and LVOA of the total organic mass obtained from the kinetic model vs. the ones from the PMF analysis are presented. Model results were obtained by using a constant enthalpy value for all organics. Note that mass fraction of LVOA\_model means here the sum of LVOA and ELVOA mass fractions obtained from the model. The colors of the data points illustrate the particle inorganic mass fraction. Correlation coefficient and equation for the line fitted to the data points to describe the agreement between the model and PMF derived organic mass fractions are given for each case.
ACKNOWLEDGEMENTS

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BELOWGROUND HYDRAULIC CONDUCTANCE CALCULATED FROM SIMULTANEOUS SAP FLOW AND XYLEM DIAMETER CHANGE MEASUREMENTS IN MATURE SCOTS PINE TREES DURING SPRINGTIME

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Keywords: DENDOMETERS, HYDRAULIC CONDUCTANCE, SAP FLOW, SOIL TEMPERATURE, SOIL WATER CONTENT.

INTRODUCTION

For plants, there can be no photosynthesis without simultaneous water loss to the atmosphere as water loss and CO2 assimilation between leaves and atmosphere are tightly coupled as both occur through the same stomatal pores in leaves. The loss of water from the leaves to the atmosphere is replaced with sap flow from the soil through the xylem transport tissue made up of woody, dead, tube-like conduits. 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 in the xylem. Soil water content is known to influence the water uptake capacity of roots from the soil as soil water potential and soil hydraulic conductance decrease with decreasing soil water content (e.g. Duursma et al. 2008). In addition to soil water content, soil temperature has been found to play a key role in the water uptake capacity of roots at low soil temperature (e.g. Running and Reid 1980, Bassirirad et al. 1991).

Xylem water relations have been studied indirectly with measurements of the minute changes in xylem diameter with precision point dendrometers. More specifically, the relative change in xylem diameter is proportional to change in xylem water potential (Irvine and Grace 1997, Perämäki et al. 2001). Here we utilize continuous measurements of xylem diameter change at the stem base with sap flow measurements to determine the belowground hydraulic conductance during spring time in mature Scots Pine trees in boreal conditions.

METHODS

Field measurements were conducted at the SMEAR II field research site in Hyytiälä. Xylem sap flow was measured with a Granier type heat dissipation sensor. Xylem diameter changes were measured with linear displacement transducers (Solartron Inc., Model AX/5-0/5, Bognor Regis, West Sussex, UK; accuracy of 1 μm) used as a point dendrometers at stem base. The belowground hydraulic conductance ($k_{bg}$), i.e. the conductance from the soil to the xylem at the point of xylem diameter change measurements was calculated to be the ratio of the daily maximal sap flow rate to the daily maximum amplitude of the xylem diameter change. The data used for the analysis was collected during spring 2013.

RESULTS

Belowground hydraulic conductance ($k_{bg}$) was a function of both soil temperature (Fig. 1) and soil water content (Fig. 2) in the springtime.
DISCUSSION AND CONCLUSIONS

The method of estimating belowground hydraulic conductance from simultaneous field measurements of sap flow and diameter change gave reasonable results over the period chosen. The belowground hydraulic conductance was found to be a strong function of temperature and soil water content. Counterintuitively, belowground hydraulic conductance increased with decreasing water content, whereas the relation between these is the opposite during summer (not shown). Data from multiple years will be analyzed in the future to draw more conclusions.
ACKNOWLEDGEMENTS

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DETECTING WEEKLY CYCLES IN PRECIPITATION AND AEROSOL CONCENTRATIONS

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Keywords: Weekly cycle, precipitation, aerosol concentration, statistical analysis.

INTRODUCTION

Weekly cycles in precipitation have been studied since the 1920s (Ashworth, 1929). Cycles corresponding to the usual working week would indicate a strong human-based effect on climate. It is known that the increase in concentration of atmospheric aerosols will also increase the concentration in cloud condensation nuclei, CCN (e.g. Kerminen et al., 2005). Variations in CCN can affect precipitation, but a clear causal connection between anthropogenic aerosols and precipitation is an active area of research. There are multiple weekly cycle studies of aerosol concentrations, precipitation and the connections between them, but the results are conflicting (Schultz et al., 2007; Bäumer and Vogel, 2007; Bell et al., 2008). The differences in outcomes may result from differences in the various analysis methods used in the different studies. Thus, understanding how to best determine weekly cycles in an arbitrary time series is crucial to determining man’s influence on the climatology of precipitation.

In this study, several statistical analysis methods for studying weekly cycles in precipitation and aerosol concentration are investigated using both simulated and measured atmospheric data. Simulated precipitation and aerosol data were used to test and compare different statistical methods used in weekly cycle studies. In many weekly cycle studies, statistical tests are often inadequate or even not suitable at all for the data they are used. Thus, the advantage in simulated data is that the uncertainties are known beforehand. The same methods were also applied to atmospheric measurements from Helsinki, Finland; San Pietro Capofiume, Italy; and London, England.

DATA AND METHODS

In weekly cycle analysis, the daily values for the investigated variables are first calculated and grouped by weekdays (7 comparable groups). Depending on the method used, values may be grouped further to weekend and weekdays (2 comparable groups). In our analysis, we tested multiple different tests used in literature: the Kruskal–Wallis test, Mann–Whitney U-test, Student’s t-test (hereafter, just t-test), a spectral analysis, chi-squared test, and Fisher’s exact test. We also compared the amplitudes of the regular 7-day week to artificial 6- and 8-day weeks. We also compared the day with the maximum amount of the investigated variable to the day with the minimum amount, by using the t-test and Kruskal–Wallis test.

For investigating the performance of the different methods, data sets of precipitation and aerosol concentration were simulated without a weekly cycle. For these, monthly averages were based on the measurements on San Pietro Capofiume (SPC). More details on the measurement site can be found in Hamed et al. (2007). The results from some of these tests for the simulated precipitation data are presented in Table 1.

As the results for precipitation in Table 1 show, the difference between the t-test and Kruskal–Wallis test is substantial when the maximum and minimum method is used. With the t-test, weekly cycles were found in over 40% of the data sets, whereas with the Kruskal–Wallis test, weekly cycles were found cycles in
only 13%. This difference can be explained by the underlying assumptions of the two tests. Whereas the
\( t \)-test assumes that the data is approximately normally distributed, the Kruskal–Wallis test does not make
this assumption. In addition, detection efficiency with \( t \)-test showed out to be insufficient with the data
including clear weekly cycle. Because neither aerosol concentration nor precipitation are normally
distributed, the \( t \)-test should generally not be used in such analyses. It can be assumed that in 5% of
randomly generated series you might see significant “cycle” with common statistical tests, which is the
case with the other methods shown in table 1.

Table 1. Number of found weekly cycles out of 1000 simulated data (with and without cycle) sets for precipitation
amount.

<table>
<thead>
<tr>
<th>Used test</th>
<th>Weekend-weekdays grouping</th>
<th>Cycles found in data with cycle</th>
<th>Cycles found in random data</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t )-test</td>
<td>Sat–Sun–Mon vs. others (2 groups)</td>
<td>302–400</td>
<td>43–51</td>
</tr>
<tr>
<td>Kruskal–Wallis test</td>
<td>Sat–Sun–Mon vs. others (2 groups)</td>
<td>960–961</td>
<td>49–57</td>
</tr>
<tr>
<td>( t )-test</td>
<td>maximum vs. minimum (2 groups)</td>
<td>890–896</td>
<td>420–430</td>
</tr>
<tr>
<td>Kruskal–Wallis test</td>
<td>maximum vs. minimum (2 groups)</td>
<td>931–940</td>
<td>131–135</td>
</tr>
<tr>
<td>Kruskal–Wallis test</td>
<td>None (7 groups)</td>
<td>998–1000</td>
<td>50–56</td>
</tr>
</tbody>
</table>

The results for measurement data are presented in Table 2. From London, we had aerosol mass density
(PM1) data instead of particle number concentration.

Table 2. Weekly cycles found from measurement data by different methods for precipitation and aerosol
concentration. Chi-squared test and Fisher exact test are for precipitation occurrence. Kruskal-Wallis test is
shortened to KW.

<table>
<thead>
<tr>
<th>Used test</th>
<th>Helsinki, aerosols</th>
<th>Helsinki, precipitation</th>
<th>London, aerosols</th>
<th>London, precipitation</th>
<th>SPC, aerosols</th>
<th>SPC, precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>KW (7 days)</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>KW (weekend vs. midweek)</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>( t )-test (weekend vs. midweek)</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Max vs. min with ( t )-test</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Max vs. min with KW</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Chi-squared (7 days)</td>
<td>-</td>
<td>No</td>
<td>-</td>
<td>Yes</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Chi-squared (weekend vs. midweek)</td>
<td>-</td>
<td>No</td>
<td>-</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>Fisher’s exact (weekend vs. midweek)</td>
<td>-</td>
<td>No</td>
<td>-</td>
<td>Yes</td>
<td>-</td>
<td>Yes</td>
</tr>
</tbody>
</table>

From the London data, many of the methods found at least weak weekly cycles for aerosols, precipitation
occurrence, and precipitation amount. If the cycle in precipitation occurrence would be strong, the
methods used in these analyses could also see the cycle in precipitation amount as the data includes large
fraction of zeros indicating days with no rain. A large number of days with no rain appears to be a concern
for the London data. The precipitation data for every measurement site was also analyzed without zeros
days without any rain), yielding no significant differences between weekdays. In all of these studied
measurement data sets, the form of the cycle clearly became more random (or it vanished completely)
when the zeros were removed from the data (Figure 1).
Somewhat surprisingly, the most significant weekly cycle was found from the aerosol concentration data from Helsinki by all methods used in this study (Figure 2). The minimum aerosol concentration occurs on Sunday, and the maximum occurs on Thursday.

CONCLUSIONS

In our analysis, many of the methods used to detect weekly cycles from aerosol or precipitation data give questionable results. The most unreliable method was the maximum–minimum method, used with \( t \)-test, which clearly overestimated the differences between weekdays for both precipitation (Table 1) and aerosol concentration (not shown). This method found significant cycles for precipitation from random time series in more than 40% of the simulated data sets when the appropriate number for cycles to occur by random is about 5%. We also showed that the \( t \)-test finds significant weekly cycles from both measurement and simulated data more often than the Kruskal–Wallis test because the Kruskal–Wallis test does not assume normality of the data.

As concluded by the data set from London (Figure 1), the zeros in the data have interesting effect to the results. Often in weekly cycle studies, it has not been mentioned if the precipitation amount cycle is
analyzed with or without precipitation-free days. Also, another interesting finding was that all methods used in our study revealed a significant difference between weekend and weekdays in aerosol concentration in Helsinki. Aerosol concentrations seem to be smaller on weekends in all measurement data sets by anomaly examination, and the only statistically non-significant weekly cycle appeared in SPC data. For precipitation, the form of the “cycles” vary. In SPC, precipitation occurrence has its maximum on weekend, when Helsinki and London have weekend minima.

Differences in significance and forms of the weekly cycles in measurement data sets may be also affected by the different lengths and quality of the data. The data from SPC covered ten years from 2002 to 2012 for both aerosol concentration and precipitation, but, after removing days with missing data and some clearly biased values, the precipitation data narrowed to 4 years only. From London, the precipitation data was from 1995 to 2015 with many fewer missing values.

To study further the causality between precipitation and aerosol concentration cycles, we would need to measure aerosol concentrations just before the rain showers. This kind of examination would take into account the decrease in aerosol concentrations caused by wet deposition. The methods used in this study have been already used in multiple studies, but in subsequent analysis we are going to test also more advanced time series analysis methods (e.g., dynamic linear models used in Mikkonen et al. (2015)). These more advanced methods will show more reliably if the cycles are truly significant and offer the possibility to study the causal assumptions between aerosols and precipitation.

ACKNOWLEDGEMENTS

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MODELLING THE SURFACE EXCHANGE OF CO$_2$ IN HELSINKI

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Keywords: CARBON DIOXIDE, EDDY COVARIANCE, URBAN, VEGETATION.

INTRODUCTION

Urban areas are major emitters for carbon dioxide (CO$_2$), which is the most important greenhouse gas in the atmosphere. Traditionally emission inventories have been used to estimate CO$_2$ emissions from cities, but they lack of spatial and temporal variability as well as of information about the effect of urban vegetation on the total emissions. Alternative method to estimate the urban CO$_2$ emissions is the usage of land surface models that account for both the anthropogenic and biogenic components. In this study, the urban net ecosystem exchange (NEE) will be modelled and evaluated against eddy covariance (EC) measurements in Helsinki, Finland.

METHODS

The land surface model used in the study is the Surface Urban Energy and Water balance Scheme (SUEWS, Järvi et al. 2011, Ward et al. 2016). Besides, the cycles of energy and water, the model has recently been updated to include the surface exchange of CO$_2$. The vegetation uptake is parameterised based on the non-rectangular hyperbola (NRH) equation, which gives the vegetation uptake relative to a light-response curve. Respiration is calculated from the air temperature. In this study, the parameters used in NRH and in the respiration model are obtained from EC measurements of CO$_2$ exchange and soil chamber measurements made in Helsinki, Finland (Järvi et al., 2012; Bellucco et al., 2016). The anthropogenic CO$_2$ emissions are tied to the anthropogenic heat emissions present in the model.

The model is evaluated against the EC observations from two sites in Helsinki (Nordbo et al., 2013; Kurppa et al., 2015). The first site, Kumpula, is located 4 km north-east from the Helsinki city centre and there around 50% of surface is covered with vegetation. This is not homogeneously divided in all wind directions, but rather certain vegetation sector can be distinguished, in addition to the road and built sectors. Data from the vegetation sector was used to obtain the parameterisations for biogenic CO$_2$ exchange components. The second site Hotel Torni is located in the Helsinki city centre where only 22% of the surface is covered with vegetation in form of street trees and a few parks. SUEWS is run within the source areas of the two EC measurement sites using measured meteorology as forcing (i.e. offline mode). The plan area fractions of different surface cover types (buildings, pavements, evergreen and deciduous trees, grass and water), and building and tree heights will be obtained from a scanning lidar (Nordbo et al., 2015).
CONCLUSIONS

The model evaluation shows that the net exchange of CO$_2$, accounting for both anthropogenic and biogenic components, can be well simulated at the more vegetated Kumpula site. Model has more problems in the densely built-up city centre site which results from the uncertainties in the modelling of the anthropogenic CO$_2$ emissions. The model is able to catch the seasonal variability in the biogenic CO$_2$ emissions correctly. Thus, the results of the comparison study indicate that SUEWS can successfully be used to simulate the surface exchange of CO$_2$. The future steps will be to run the model spatially in Helsinki city centre in order to study the spatial variability of CO$_2$ exchange in Helsinki and estimate the effect of vegetation to the carbon balance in a city scale.

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REFERENCES


THE EFFECT OF PINE WEEVILS ON VOC EMISSIONS FROM SCOTS PINE SAPLINGS

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Keywords: HERBIVORE INDUCED PLANT VOLATILES, VOLATILE ORGANIC COMPOUNDS.

INTRODUCTION

Plants emit a large variety of volatile organic compounds (VOCs) into the atmosphere (Guenther et al., 1995). There are biotic and abiotic stress factors that affect both the chemical composition and emission rates of VOCs (Holopainen and Gershenzon, 2010). One class of VOCs, called herbivore induced plant volatiles (HIPVs), are produced by plants in response to herbivory. One of the primary functions of HIPVs is to provide plants with direct and indirect protection against herbivores. Many VOCs are produced and emitted by intact plants, called constitutive emissions. In contrast, HIPVs refer to the specific VOCs that are produced after herbivore damage. Some of HIPV emissions can be produced by intact plants with lower quantities, as well. The aim of this study was to measure and quantitatively describe HIPV emission dynamics from Scots Pine (Pinus sylvestris) after the saplings were exposed to bark borer herbivory.

METHODS

To study HIPV emission dynamics, 7-year old Scots pine saplings were exposed to four bark feeding-pine weevils (Hylobius abietis) in the laboratory for two days. Four set of experiments were conducted, and each experiment involved two trees, one control and one treatment tree. Each tree was placed inside 40 x 100 cm Teflon® bags, and purified air was continuously flushed through the bags at a flow rate of 3.0-4.0 l min⁻¹. Furthermore, additional PAR light was provided for the trees from 6 A.M. to 6 P.M., in order to simulate a natural daily cycle.

The emission from both trees were continuously measured by proton transfer reaction-time-of-flight mass spectrometry (PTR-ToF-MS, PTR-TOF 8000, Ionicon Analytik, Austria) using an automated valve switching system. PTR-ToF-MS enables fast and continuous monitoring of plant emissions before and after herbivore damage. To supplement PTR-ToF-MS measurements, cartridge samples (Tenax TA/Carbograph 5TD material, MARKES international, United Kingdom) were collected twice per day, and analysed offline via thermodesorption- gas chromatography- mass spectrometry (TD-GC-MS, TD, Perkin-Elmer ATD 400 Automatic Thermal Desorption system, USA; GC-MS, Hewlett Packard, GC 6890, MSD 5973, USA).

Before the treatment tree was exposed on herbivores, its baseline VOC emission rates were measured for several days. Herbivore exposure was conducted by placing the herbivores inside a mesh enclosure that was attached to the tree trunk. Control tree was handled similarly as treatment tree, except that control tree was not exposed on herbivores. After pine-weevils were removed, post-treatment period was monitored for 2-14 days to see whether the increased emissions remained elevated or not after active feeding of herbivores.
CONCLUSIONS

The results from this study showed that the most dramatic change in emissions, caused by pine weevils was observed for monoterpene emissions. Other compounds like sesquiterpenes had elevated emissions as well, but a lesser extent. As Figure 1 shows that the effect of pine weevils on sesquiterpene emissions was much lower, and it occurred more slowly compared to monoterpene emissions. Figure 1 also demonstrates that monoterpene emissions increased by over 100-fold due to pine weevil feeding. Furthermore, it can be seen that the emissions remained elevated above pre-treatment values after pine weevils were removed, during the whole post-treatment monitoring period (48 hours).

![Figure 1. The change in emission rates of monoterpenes (upper panel) and sesquiterpenes (lower panel) due to pine weevil feeding, monitored by PTR-ToF-MS from one experiment. Black circles are data points measured from treatment tree, and grey circles are the data points measured from control tree. At time 0 the treatment was started, and at time 50 the treatment was stopped.]

TD-GC-MS results showed that the mono- and sesquiterpene emission profiles were dominated by the same compounds during each experimental phase (pre-treatment, active feeding, post-treatment). This demonstrates that pine weevil feeding did not clearly induce emissions of any major new compounds from Scots pine saplings. Furthermore, this suggests that the mechanism causing increased emissions is mechanical damage of stem tissue exposing storage resin ducts.

In a changing climate increasing frequency and severity of herbivore outbreaks are expected. This study demonstrates that this increase will lead to significantly higher monoterpene emissions from forests.
However, it is important to note that these results apply only to pine weevils, and other herbivores can have very different effect on plant emissions.

ACKNOWLEDGEMENTS

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Aerosol mass concentration measurements at SMEARII

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Keywords:  Atmospheric aerosol particles, long-term measurements, mass concentration

INTRODUCTION

Atmospheric nucleation can happen via molecular clustering and it is followed by cluster activation for enhanced growth. Freshly-formed particles grow by condensation when different vapors condense onto the particle surfaces or the particles collide and stick together, in a process called coagulation. When aerosol particles grow further to sizes where they can act as cloud condensation nuclei, they start to have effect on climate. The main objective is to contribute to the reduction of scientific uncertainties concerning global climate change issues, particularly those related to aerosol cloud interactions (IPCC 2013). The SMEAR II is a 20-year-old research station in Scots pine stand for studying the atmosphere and forest/lake/wetland ecosystem interactions. Currently, the newly-formed 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). Here, we are comparing the three methods for aerosol mass quantification at SMEARII. First aerosol direct mass measurements by cascade impactor started in 1996 (Mäkelä et al., 1997) and are still ongoing. The second indirect method for aerosol mass quantifying by aerosol number size distribution was possible from 2004, when there have been the complete measurements of airborne particles during their lifetime as aerosol. Lately from 2011 there have been on-line mass measurements based on beta-attenuation. Here, we compare the mass concentration of three different size classes with particle diameter below 10 (PM10), 2.5 (PM2.5) and 1 (PM1) µm. We measure these internationally standardized size classes e.g. for consistent comparison with measurement stations and as they are important when considering the health effects of particulate matter and these particles deposition in our body (Marple et al., 1983). It is really challenging to measure the top quality mass concentration in boreal forest, where these concentrations are usually subsequent low 2-6 µg/m$^3$ (Laakso et al., 2003), e.g. in comparison in urban areas the values are usually at least 10 times higher.

METHODS

The mass measurements are performed at SMEAR II (Station for Measuring Forest Ecosystem-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 continuously and comprehensively measure forest ecosystem-atmosphere interactions (Kulmala et al., 2014). Hyytiälä is a rural and background site with low local particle matter emissions. All compared equipments for mass measurements are located at the Hitu-hut and the sampling lines are located in forest (4-8 m) from ground level (Figure 1).
Cascade impactor has been one of the aerosol science masterpiece equipment used for several decades (May, 1945). A cascade impactor is made up of a number of classification stages consisting of a nozzle and an impaction plate. In each stage, an aerosol stream passes through the nozzle and impinges upon the plate. Particles in the aerosol stream having large enough inertia will impact upon the plate, and smaller particles will pass as an aerosol onto the next stage. By designing each successive stage with higher aerosol velocities in the nozzle, particles with the smaller diameter will be collected at each stage. Particles too small to be collected in the last stage are generally collected on an after-filter (Marple et al., 1993). Since, 1996 we have used a three stage Dekati® PM10 impactor, which measures < 10 µm (PM10), 2.5-10 µm PM2.5 and >1 µm PM1 mass concentrations. The impactor sampling line was placed on the cottage roof 5.5 m from the ground level (Figure 1, sampling line 4).

The aerosol mass for different size classes PM1, PM2.5 and PM10 was also quantified by measuring its number size distributions by Differential Scanning Mobility Sizer (DMPS) and Aerosol Particle Sizer (APS). The twin-DMPS consist of a long and short Differential Mobility Analysers (DMA, Viennese) and two condensation particle counters (CPC, TSI3025 and 3775). The DMPS (Flagan, 2001) measures number size distribution in the range of 3-1000 nm. The APS (TSI) is measuring aerodynamic particle size distribution from 0.5-20 µm (Peters, 2006). To have a consistent and comparable particle size with DMPS, we calculated stokes diameter from aerodynamic diameter with the following equation:

$$\rho_p d_s^2=\rho_a d_a^2,$$

where $d_s$ is Stokes diameter, $\rho_p$ is particle density (here we used 1.5 g/cm$^3$), $d_a$ is aero diameter, $\rho_a$ is particle aerodynamic density. From the resulted combined size distribution from both equipment the mass concentration was calculated from:

$$m=\rho_p((\pi d_p^3)/6)$$

For the PM10, we compared three different methods impactor, DMPS+APS and Synchronized Hybrid Ambient Real-time Particulate Monitor SHARP (Thermo Scientific, Model 5030), which is a synchronized hybrid ambient "real-
time” particulate monitor. The SHARP Monitor combines light scattering photometry and β-ray attenuation for continuous PM10 measurement. The SHARP utilizes proprietary digital filtering to continuously mass calibration of the nephelometric measurement of PM10. The SHARP was used with a flow rate of 16.7 L/min and with the fixed sampling temperature of 45 °C.

RESULTS

Here we present the PM1, PM2.5 and PM10 mass concentration measured at Hyytiälä during 2012-2014. We have distributed the results by year and by four seasons: Winter (December-February), Spring (March-May), Summer (June-August) and Autumn (September-October).

In Table 1 is presented the average mass concentration in 2012 (a) and 2014 (b) with their uncertainties. First we can see that the mass concentration is subsequent low in Hyytiälä, from 2.3 to 9.2 μg/m³, as expected for the rural conditions (Laakso et al., 2003). The mass concentration varied from 2.3 to 5.8 for PM1, from 3.5 to 6.5 for PM2.5 and from 3.7 to 9.2 for PM10. Besides the winter 2012, the mass values measured with the impactor are systematically slightly higher compared to the values calculated from DMPS and APS measurements. The systematic positive error can be caused e.g. due to the condensed water on the collection membranes or decrease of the impactor flow, which causes the cut point diameter to increase. Clear errors caused by a dust particle or some organic matter from forest have been filtered from the data. When we compare the values from SHARP to impactor they are always, with one exception (summer 2012), lower than the ones measured by impactor. One explanation to this can be that the low volatility species (such as organonitrates) were evaporated, because the SHARP sampling line was heated to 45 °C. Also, the SHARP detection limit is quite high (0.5 μg/m³) for the Hyytiälä rural and boreal forest conditions, where the particle concentrations are really low. This can also lead to underestimation of the mass concentrations.

**Table 1.** Mass concentrations μg/m³ for 2012 (a) and 2014 (b) measured with the different methods for each size classes PM1, PM2.5 and PM10.

<table>
<thead>
<tr>
<th></th>
<th>(a) Year 2012</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM1: Impactor</td>
<td>5.3 ± 0.6</td>
<td>3.0 ± 0.4</td>
<td>3.9 ± 0.3</td>
<td>2.6 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>PM1: DMPS</td>
<td>5.4 ± 0.5</td>
<td>2.8 ± 0.3</td>
<td>3.7 ± 0.2</td>
<td>2.3 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>PM2.5: Impactor</td>
<td>6.4 ± 0.8</td>
<td>4.1 ± 0.6</td>
<td>4.8 ± 0.3</td>
<td>3.6 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>PM2.5: DMPS+APS</td>
<td>7.7 ± 0.8</td>
<td>3.9 ± 0.3</td>
<td>4.2 ± 0.3</td>
<td>3.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>PM10: Impactor</td>
<td>6.9±0.8</td>
<td>6.0 ± 0.9</td>
<td>6.5 ± 0.6</td>
<td>4.6 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>PM10: DMPS+APS</td>
<td>6.4 ± 0.8</td>
<td>4.8 ± 0.4</td>
<td>4.9 ± 0.4</td>
<td>3.9 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>PM10: SHARP</td>
<td>6.5 ± 0.8</td>
<td>5.2 ± 0.4</td>
<td>7.7 ± 0.6</td>
<td>5.6 ± 0.7</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>(b) Year 2014</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM1: Impactor</td>
<td>4.1 ± 0.4</td>
<td>4.6 ± 0.7</td>
<td>5.3 ± 0.5</td>
<td>5.8 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>PM1: DMPS</td>
<td>3.4 ± 0.3</td>
<td>3.3 ± 0.5</td>
<td>4.6 ± 0.5</td>
<td>4.3 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>PM2.5: Impactor</td>
<td>5.0 ± 0.4</td>
<td>6.5 ± 1.1</td>
<td>6.4 ± 0.6</td>
<td>3.4 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>PM2.5: DMPS+APS</td>
<td>5.0 ± 0.6</td>
<td>5.0 ± 0.7</td>
<td>5.3 ± 0.5</td>
<td>3.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>PM10: Impactor</td>
<td>5.4 ± 0.5</td>
<td>9.2 ± 1.7</td>
<td>8.1 ± 0.8</td>
<td>8.1 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>PM10: DMPS+APS</td>
<td>5.3 ± 0.6</td>
<td>5.9 ± 0.8</td>
<td>7.2 ± 0.8</td>
<td>7.5 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>PM10: SHARP</td>
<td>3.7 ± 0.4</td>
<td>5.1 ± 0.7</td>
<td>5.7 ± 0.7</td>
<td>5.4 ± 0.5</td>
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</table>

Overall correlations between different measurement techniques with these three size classes are shown in table 2. We can see that the smaller the particle size is, the better the measurement techniques are correlated. The correlations at sizes PM1 and PM2.5 are varying between 0.72 and 0.85. The best correlation 0.85 is between impactor and DMPS at smallest size range PM1. The smallest correlation 0.44 is between the impactor and SHARP in 2012. The simplest guess can be that the SHARP measurement started at that year and there were many operational challenges in the beginning. Other reason can be that the heating of the sample line evaporates some low volatile species, or detection limit, which can systematically ignore small masses below detection limit as mentioned earlier. However, we also need to be critical for the impactor measurements, because there still might be humidity in the samples while they are weighted, or the cut point is shifted slightly for larger particles.
Table 2. Correlations and P values between impactor and listed methods for the different size classes for separate years 2012, 2013 and 2014 as well for the years 2012-2014.

<table>
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<tbody>
<tr>
<td>PM$_1$ (DMPS)</td>
<td>0.85 (1 \times 10^{-37})</td>
<td>0.75 (1 \times 10^{-25})</td>
<td>0.84 (3 \times 10^{-38})</td>
<td>0.82 (6 \times 10^{-99})</td>
</tr>
<tr>
<td>PM$_{2.5}$ (APS + DMPS)</td>
<td>0.74 (3 \times 10^{-24})</td>
<td>0.72 (1 \times 10^{-22})</td>
<td>0.76 (1 \times 10^{-27})</td>
<td>0.75 (7 \times 10^{-75})</td>
</tr>
<tr>
<td>PM$_{10}$ (APS + DMPS)</td>
<td>0.59 (1 \times 10^{-13})</td>
<td>0.68 (1 \times 10^{-19})</td>
<td>0.69 (3 \times 10^{-21})</td>
<td>0.68 (5 \times 10^{-56})</td>
</tr>
<tr>
<td>PM$_{10}$ (SHARP)</td>
<td>0.44 (5 \times 10^{-7})</td>
<td>0.62 (1 \times 10^{-14})</td>
<td>0.78 (2 \times 10^{-29})</td>
<td>0.60 (2 \times 10^{-38})</td>
</tr>
</tbody>
</table>

DISCUSSION

We have measured the particle mass concentration with particle size ranges <1 μm (PM1), 1-2.5 μm (PM2.5) and > 10 μm (PM10). The overall concentration from 2012 to 2014 varied from 1 to 14 μg/m$^3$ for PM1 and from 1 to 20 μg/m$^3$ for PM2.5 and PM10. We compared three methods: direct gravimetric impactor, mass calculated from size distribution (DMPS, APS) and mass measured online by beta-attenuation (SHARP). The smaller the particles were, the better the methods correlated. In conclusion, it is reasonable to have at least two methods measuring the mass concentration to maintain good data quality and comparison.

ACKNOWLEDGEMENTS


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PARTICIPATION IN COUPLED MODEL INTERCOMPARISON PROJECT PHASE 6

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Keywords: CMIP, AERCHEMMIP, CLIMATE MODEL.

INTRODUCTION

Coupled Model Intercomparison Project (CMIP) is an internationally coordinated multimodel climate experiment, initiated by a few modelling groups in the 1990s. The most recent CMIP (Phase 5) included over 25 modelling centres and over 60 distinct climate models. The CMIP process is not governed by the International Panel on Climate Change (IPCC). Nevertheless, ongoing CMIP6 is expected to support the Sixth Assessment Report (AR6) of IPCC which is to be released during 2020-2021.

For the first time, Finnish research groups are fully committed to carrying out CMIP simulations on national infrastructure. Groups from University of Helsinki (UHEL) and Finnish Meteorological institute (FMI) are committed to AerChemMIP experiments through the EC-Earth consortium. The participation in AerChemMIP is done jointly with the Royal Netherlands Meteorological Institute (KNMI). CMIP6 protocol requires that all participating model groups also complete the Diagnosis, Evaluation and Characterization of Klima (DECK) and historical simulations (Figure 1).

Participation in CMIP allows Finnish groups to be in the forefront of climate research, and establishes a direct link between ATM FCoE and future climate assessments.

DECK AND CMIP HISTORICAL SIMULATIONS

The DECK simulations consist of four, well established baseline experiments (Eyring et al., 2016). In the atmospheric model intercomparison project (amip) simulation, the sea surface temperatures and the sea ice concentrations are prescribed according to observations, allowing for the evaluation of the atmospheric and land components of the model. The pre-industrial control (piControl) simulation aims to produce a near-equilibrium climate state using the pre-industrial conditions from the year 1850. In addition to being a control simulation for other experiments, it can be used to study the naturally occurring variability of the climate system. The last two DECK simulations are climate change experiments based on the piControl simulation. In the abrupt quadrupling of CO\textsubscript{2} concentration (abrupt-4×CO\textsubscript{2}) simulation, the initial CO\textsubscript{2} level of the simulation is four times that of the annual mean value of 1850 while in the 1 % per year CO\textsubscript{2} concentration increase (1pctCO\textsubscript{2}) simulation the CO\textsubscript{2} level is increased annually by 1 %. The abrupt-4×CO\textsubscript{2} simulation can be used to characterise radiative forcing and indirect changes due to warming while the 1pctCO\textsubscript{2} has been useful in the analysis of model transient climate response.

The simulations that make up the DECK provide continuity across the different phases of CMIP. All of them were a part of CMIP5 and all bar abrupt-4×CO\textsubscript{2} simulation were included even in the earlier phases of CMIP. In the future phases of CMIP, additional simulations can be added to the DECK if they become enough well established. All models participating in the CMIP6 are required to perform the DECK simulations together with a prescribed historical simulation, allowing for model characterisation and evaluation. The historical CMIP simulation is based on the piControl simulation but has observation-based, evolving forcings. The historical simulations allow for the assessment of the capability of the model to simulate climate. The minimum number of simulated years ranges from 36 in amip to 500 in piControl. Longer runs and the generation of ensembles are recommended for some experiments.
AEROSOLS AND CHEMISTRY MODEL INTERCOMPARISON PROJECT (AERCHEMMIP)

The AerChemMIP, one of the 21 CMIP6-endorsed Model Intercomparison Projects (MIPs), concentrates on the impacts of aerosols and chemically reactive gases (Collins et al., submitted). The project contains 35 experiments, set up in order to answer four different research questions. The first concerns the contribution of anthropogenic aerosols and reactive gases to global effective radiative forcing and regional climate change over the historical period. It is answered using three historical coupled-ocean experiments, seven historical experiments with prescribed sea surface temperature, and 10 timeslice historical experiments with prescribed sea surface temperature. The second research question asks how future policies affect the near-term climate forcers and associated climate impacts, and is studied through two future simulations with coupled ocean model and seven future simulations with prescribed sea surface temperature. The timeslice historical experiments used with the first research question are also used to answer the third research question: how does radiative forcing depend on uncertainties in anthropogenic emissions? The fourth research question studies the quantification of climate feedback occurring through changes in natural emissions using six experiments with doubled natural emissions.

The experiments in AerChemMIP are tiered and only tier 1 is overseen by the CMIP panel while participation in tiers 2 and 3 is encouraged (Eyring et al., 2016). The AerChemMIP participation of UHEL together with collaborators at FMI and KNMI will consist of experiments from tiers 1 and 2, excluding certain experiments due to model restrictions.
REQUIRED INFRASTRUCTURE

UHEL and FMI teams will participate in CMIP6 with EC-Earth climate model (Hazeleger et al., 2012). The EC-Earth consortium is comprised of over 30 partners from over ten countries. EC-Earth includes atmospheric model IFS, ocean model NEMO, sea ice mode LIM and land-vegetation model LPJ-GUESS. In addition, atmospheric chemistry and aerosols are simulated by transport model TM5. Submodels are coupled with the OASIS coupling software. The IFS model will be run with T255 resolution (~80 km) and 91 vertical levels, whereas the aerosol-chemistry is simulated in coarser horizontal resolution of 3x2 degrees with 34 levels.

The DECK and CMIP historical simulations require at least 1,001 simulated years (Eyring et al., 2016) while the simulation of AerChemMIP tier 1 and tier 2 experiments requires 1,628 and 1,265 simulated years respectively. This translates to millions of CPU hours on the platform where the simulations will be carried out: the Sisu supercomputer (Cray XC40) of CSC. Due to the relatively large computational requirements of the project, the resources have been applied through CSC’s Grand Challenge framework. In addition to computing resources, the project requires significant data storage resources.

From the ~1 gigabyte of data produced in CMIP1, the multi-model data to be archived in CMIP5 had already increased to 3-4 petabytes. Preliminary estimates for total data produced by the upcoming CMIP6 experiments are in the range of 350 PB to 3 EB. The data produced by the DECK, the historical simulations, and the AerChemMIP will be distributed through the Earth System Grid Federation (ESGF) and it will be freely available after registration (Eyring et al., 2016; Collins et al., submitted).

The ESGF is an international collaborative effort towards the development of software infrastructure for the study of climate change (Cinquini et al., 2014). The ESGF system is composed of nodes that are distributed around the world and communicate through a peer-to-peer protocol. Each node can, depending on its configuration, take part in data publication, indexing, user authentication, and in providing computational capacity. Even though the data are distributed to different ESGF nodes, they can be accessed as if in a single location. The Finnish ESGF node will be set up by CSC.

The model infrastructure is being finalized: EC-Earth will receive last updates in model code during 2016, while the coupled model system is being prepared for production simulations. First CMIP6 datasets are expected to emerge during the first half of 2017. After post-processing and quality control, first selected datasets are distributed through the ESGF node, allowing international research community to begin a new phase of climate assessments.

ACKNOWLEDGEMENTS

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GREENHOUSE GAS CONCENTRATION OBSERVATIONS FROM FINNISH STATIONS AND IDENTIFICATION OF LOCAL SOURCES IN HELSINKI

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Keywords: GREENHOUSE GASES, METHANE, MEASUREMENTS.

INTRODUCTION

Finnish monitoring stations have produced several years of high resolution atmospheric composition observations. The observed greenhouse gases carbon dioxide (CO\textsubscript{2}) and methane (CH\textsubscript{4}) are sensitive to anthropogenic sources from European hotspots, while also showing natural signals from forests and wetlands. CH\textsubscript{4} is interesting for its large unknowns; globally, it has proved difficult to simulate. These observations can be used to constrain wetland models and anthropogenic emission inventories in Northern Europe. Cases from Russia (Moscow, gas and oil production sites) are common.

METHODS

The sites cover marine, continental, urban and remote locations (Kilkki et al. 2015). Concentrations of CO\textsubscript{2}, CH\textsubscript{4} and carbon monoxide (CO) were measured by cavity ring-down spectrometers using calibration gases traceable to WMO/CCL scale.

To relate local signals of CH\textsubscript{4} at the urban site Kumpula to nearby emissions, we ran backward-dispersing footprints with the chemistry transport model SILAM (Sofiev et al 2006). The model was run in Eulerian mode at 500 meter resolution for hourly emissions in 2011. The largest source is Ämmässuo landfill 24 km west from the site, emitting thousands of tons of methane a year. In the model, it was represented as a point source to be multiplied with the footprint. A positive relationship to observed anomalies can be expected.

Figure 1. Observation stations
CONCLUSIONS

Both CO\textsubscript{2} and CH\textsubscript{4} observations are highly correlated in long-range transport (Figure 2). CO\textsubscript{2} rises 10 ppm above marine boundary layer levels and CH\textsubscript{4} up to 50 ppb.

The stations are correlated with an expected variogram (Figure 3). The correlation varies from about r=.8 for 140–220 km to about r=.5 at 900 km. Mean square difference is higher only for Kumpula, indicating that about a third of the squared difference is explained by a difference in mean, i.e. local emissions.

Carbon monoxide concentration could identify large anomalies presumably emitted from urban sources (Figure 4). Many high variability cases remained in the case of CH\textsubscript{4}, indicating local influence from the direction of the landfill (~280°) and possibly other sources such as a sewage water treatment plant (~35°). Modelled sensitivity to the nearby landfill had almost no relationship to observed anomalies. The highest sensitivities are found at night-time, and although we selected relatively dynamic conditions (wind > 3 m s\textsuperscript{-1}), the model cannot capture the complexity of flow in these cases. We are currently conducting transport and inversion modelling in larger scales, where errors tend to even out and emission inventories can properly be constrained.

Figure 2. Monthly mean atmospheric GHG afternoon (1200–1600 hours) concentration observations. Marine boundary layer means for the latitude 62°N provided by NOAA ESRL Global Monitoring Division (http://esrl.noaa.gov/gmd/).

Figure 3. Variogram (mean squared difference, variance) of CH\textsubscript{4} observations at the four stations. Zonally averaged NOAA backgrounds were subtracted from the observations.
Figure 4. Wind-direction dependence of filtered and unfiltered CO$_2$ and CH$_4$ observation anomalies. Baseline is the corresponding seasonal time series (afternoon averages least squares -fitted to three polynomial and three harmonic components over the entire measurement period). “High” cases refer to 95$^{th}$ percentile and above. Modeled cases (blue) are from 2011 only.

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REFERENCES


10 YEARS OF CLOUD DROPLET ACTIVATION DATA FROM PALLAS ATMOSPHERE-ECOSYSTEM SUPERSITE IN SUB-ARCTIC FINLAND

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Keywords: AEROSOL-CLOUD INTERACTIONS, DMPS, LONG TIME SERIES.

INTRODUCTION

The interactions between aerosol particles and clouds cause the largest uncertainty in our estimate of present day radiative forcing compared to pre-industrial time (IPCC, 2013). The most important question is cloud formation, specifically which particles activate into cloud droplets and which do not (McFiggans et al., 2006). This has been studied a lot in simulation chambers and in ambient air during measurement campaigns (eg. Sun et al., 2006). Continuous measurements with ccn-counters have allowed us to investigate the particles’ ccn-potential, i.e. which ambient particles would activate in a given supersaturation of water in the air (eg. Burkart et al., 2011). This approach, however, does not tell which particles really do activate in the formation process in a real cloud, as the supersaturation can vary significantly as function of time and location even within a single cloud.

An indirect method to investigate the number and size distribution of activated particles is to measure the particles inside a cloud simultaneously via two inlets, one allowing the cloud droplets to enter the measurements and one blocking them. Once water is evaporated from both particle populations, they are comparable and the difference between them refers to those particles that have been activated into cloud droplets (Komppula et al., 2005).

Conducting this type of measurements at a mountain or hill top site (being frequently within cloud) allows long time series of ambient cloud droplet activation data. This enables investigation of seasonal and inter-annual variation and trends in climate-relevant time scales. We have measured particle number size distribution (PNSD) with this method at Sammallunturi measurements site (24.12°, 67.97° N, 565 m asl), located at a hill top at Pallas Atmosphere-Ecosystem Supersite (Lohila et al., 2015) in Finnish Lapland for more than a decade. Our visibility data started at 1995, PNSD data without cloud droplets in 2000 and with cloud droplets in 2005. All these measurement series are ongoing and continuous except for short gaps.

METHODS

There are two parallel Differential Mobility Particle Sizers (DMPS) at the site, measuring the number concentration and dry size distribution of atmospheric aerosol particles. One DMPS is connected to gas line inlet, which prevents particles larger than about 5 µm from entering the sample line. The other DMPS is connected to a total air inlet with a much larger, yet undefined, cut-off diameter. After each inlet the particles are dried to evaporate any water in them. Subtracting the gas-line PNSD from the total air-line PNSD gives the PNSD of those particles that have activated into cloud droplets. Aerosol particles with very small diameter are not expected to activate into cloud droplets but can be scavenged by the larger droplets or evaporated during the evaporation of water in the particles (Komppula et al., 2005). Therefore only particles with diameter ($D_p$) larger than 50 nm are included in this analysis. We performed the data analysis for hourly-averaged data. Periods when visibility or particle number-size-distribution were changing significantly during the hour were excluded from the analysis.
The measurement site is located on a hill top, about 300 m above the surrounding lowlands. The presence of a cloud at the measurement site was based on visibility, and defined as horizontal visibility < 1000 m. This is in line with the synoptic definition of fog (AMS, 2013), and is also supported by particle activation measurements. Activated fraction of particles (Act%) was close to zero during higher visibility, but increased sharply when visibility was below 1000 m (Figure 1).

Figure 1. Mean activated fraction of three particle diameter ranges as function of visibility.

RESULTS

The site was found to be inside cloud (in-cloud time, $T_{\text{cloud}}$) for 23 % of time during the entire time span of the measurements. Annual mean $T_{\text{cloud}}$ varied from year to year, ranging from 16 % in 2003 to 29 % in 2012 (Figure 2). The inter-annual variation shows signs of a roughly sinusoidal pattern on longer time scale, with a period of 8 years. When only the time periods with cloud but no precipitation were included, this pattern remained.

Figure 2. Annual fraction of time for which the measurement site was inside cloud, and annual mean particle number concentration.
There was also a clear seasonal pattern in $T_{\text{cloud}}$, the measurement site being inside cloud most often ($T_{\text{cloud}} = 46\%$) in November and least often ($T_{\text{cloud}} = 9\%$) in June (Figure 3). This pattern was similar for all the measured years, and remained when precipitating clouds were removed.

Aerosol particle number concentration, $N_p$, (for particles with diameter between 50 nm and 500 nm) showed a similar inter-annual pattern at the site when compared to $T_{\text{cloud}}$, with high and low annual mean values of $N_p$ coinciding with high and low annual mean values of $T_{\text{cloud}}$, respectively (Figure 2). The seasonal patterns of $T_{\text{cloud}}$ and $N_p$ were, however, very different (Figure 3). Where $T_{\text{cloud}}$ peaks strongly in fall, $N_p$ peaks in summer. This also means that even though the low clouds reaching the site are most frequent in fall, the more rare summer clouds have highest number of potential ccn. The high particle number concentration in summer clouds leads to increase of $D_{50}$ activation diameter (diameter at which 50% of particles with that diameter activate), which is shown in Figure 4. Also the optically thickest clouds (in-cloud periods with lowest visibility) were observed in summer.

![Figure 3. Mean monthly patterns of time for which the measurement site was inside cloud and particle number concentration.](image)

![Figure 4. Mean monthly pattern of $D_{50}$ activation diameter during times when the measurement site was inside cloud.](image)
CONCLUSIONS

This research demonstrates that visibility can be used as a proxy for the measurement site being inside a cloud, and that 1000 m visibility is a good separation criterion between in-cloud and outside-cloud periods. We observed signs of similar inter-annual patterns in cloudiness and particle number concentration. The seasonal patterns, however, were very different from each other. Even though highest in-cloud time fractions were observed in the fall months, the highest number concentrations of activated particles and highest $D_{50}$ activation diameters were observed in summer.

ACKNOWLEDGEMENTS

This work was supported by the EC FP7 project BACCHUS (grant 603445) and H2020 project ACTRIS-2 (grant 654109), by Academy of Finland (project 272041) and by Kone Foundation. We also want to acknowledge all those who have made the data collection possible.

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SENSITIVITY OF THE URBAN LAND SURFACE MODEL SUEWS TO WATCH FORCING DATA

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Keywords: URBAN WATER BALANCE, PRECIPITATION, LAND SURFACE MODEL, DOWNSCALING, SUEWS.

INTRODUCTION

The objective of this study is to assess the impact of reanalysis forcing data, and its downscaling on the performance of an urban land surface and water balance model (SUEWS, Järvi \etal, 2011, 2014; Ward \etal, 2016) in Vancouver, Canada and London, UK. With ongoing global urban growth and development, there is an increasing need for detailed modelling of urban water balance components especially in areas where no observations exists, or under future urbanization scenarios. In this study we use the WATCH WFDEI (Weedon \etal, 2014) reanalysis data to force the model (SUEWS) (Järvi \etal, 2011, 2014; Ward \etal, 2016). The precipitation of the reanalysis data is corrected using bias correction with quantile mapping (BCQM) and the sensitivity of the model to different meteorological parameters of the reanalysis data is examined.

METHODS

Version V2016a of the Surface Urban Energy and Water Balance Scheme (SUEWS) is used in this study. The model is run with a recommended 5-min time step. The meteorological forcing data is given in hourly resolution and it is interpolated to the needed 5-min resolution within the model. SUEWS has seven surface types (paved, buildings, evergreen trees/shrubs, deciduous trees/shrubs, grass, bare soil and water). The meteorological variables required to force the model are wind speed ($U$), relative humidity ($RH$), air temperature ($T_a$), pressure ($p$), precipitation ($P$) and incoming solar radiation ($K_{down}$).

SUEWS is run in two study sites (Vancouver-Oakridge and Vancouver-Sunset) in Vancouver and in one site in London. Both cities experience maritime temperate climates, but have different amounts of precipitation. In Vancouver, the two suburban neighbourhoods differ in their lot and building size and land cover. Vancouver-Sunset is more densely populated and the surface cover fraction of impervious surfaces is 68\%, whereas in Vancouver-Oakridge the fraction of impervious cover is 44\%. Also the amount of irrigation varies between the sites affecting the water balance. The two sites are approximately 3 km apart on fairly flat terrain. The simulated area in London is located in the central business district, Westminster, with high amount of impervious surface (81\%) and little vegetation (5\%). The area has a large daytime population and high volume of traffic (Greater London Authority, 2015). There is no irrigation at the studied area in London.

Observations for both cities are used for model evaluation, forcing and to compare and correct the reanalysis data used to force the model. Modelled evaporation is compared with the eddy covariance (EC) observations at Vancouver-Sunset (Christen \etal, 2011) and London (Kotthaus and Grimmond, 2014a,
Long-term observations needed for the BCQM correction were made with tipping bucket rain gauges at Vancouver-Oakridge (Environment Canada, 2015) and St. James's Park (Met Office, 2015). The WATCH Forcing Data ERA-Interim (WFDEI) (Weedon et al., 2014) are used to force the model. The WFDEI data are derived from ERA-Interim reanalysis product for hydrological modelling purposes. The spatial resolution of the dataset is 0.5º x 0.5º and the temporal resolution is 3 h. The precipitation of the WFDEI data is corrected using the bias correction with quantile mapping (BCQM, Kokkonen et al. 2016). The correction method is similar to the one used in Räisänen and Räty (2013).

The model is forced using both hourly measured data (from now on control run) and WFDEI reanalysis data. The latter includes both BCQM corrected and uncorrected WFDEI data. The sensitivity of the model to the reanalysis data is examined by changing one variable in the measured forcing data to the reanalysis data at a time. The performance of the model is evaluated by comparing model outputs (evaporation and surface runoff) against eddy covariance observations.

For London and Vancouver-Sunset a full year is simulated (2012 and 2009, respectively) for the EC footprint area and Vancouver-Oakridge is simulated for 22 January – 31 December 1982 for the water monitoring area (Christen et al., 2009).

CONCLUSIONS

At all three sites precipitation has the largest impact of the meteorological variables on modelled evaporation and runoff when compared to the control run (Kokkonen et al., 2016). Changing the observed precipitation to WFDEI precipitation overestimates the modelled cumulative evaporation 14–26% and runoff 7-39% when compared to the control run. Other meteorological variables (U, T, K_{down} and p) had only a minor effect on the model outputs.

The BCQM correction decreased the overestimation of precipitation at all studied sites. The BCQM corrected precipitation replaced in otherwise observed forcing data decreases the overestimation of evaporation by 4–15% when compared to the evaporation given with uncorrected precipitation. The BCQM corrected precipitation is used the difference in runoff decreases by 0–20% compared to the difference with uncorrected WFDEI data. Both runoff and evaporation are brought closer to the values of the control run after the BCQM correction. The BCQM correction also decreases the hourly RMSE of evaporation when compared to the EC observations. With the BCQM corrected precipitation, the WFDEI forcing data can be used to model urban hydrology and land surface processes.

ACKNOWLEDGEMENTS

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SEASONAL VARIATION OF SUB-3 NM PARTICLE CONCENTRATIONS IN BOREAL FOREST AND URBAN SITE IN FINLAND

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Keywords: CLUSTERS, NANOPARTICLES, NUCLEATION, NEW PARTICLE FORMATION.

INTRODUCTION

In recent years, the development of condensation particle counters (CPCs), such as a Particle Size Magnifier (PSM; Vanhanen et al., 2011), has enabled to directly detect sub-3 nm atmospheric particles. Consequently, there is an increasing number of studies reporting sub-3 nm particle concentrations measured at different sites around the world (Kulmala et al., 2013; Rose et al., 2014; Yu et. al., 2014; Xiao et al., 2015; Kontkanen et al., 2016a; Kontkanen et al., 2016b). The results indicate that sub-3nm particle concentration varies strongly between different environments. However, as the measurements have been conducted only during relative short measurement campaigns, the seasonal variation of sub-3 nm particle concentration has not yet been revealed. In this study, the measurements of sub-3 nm particle concentrations were conducted in two Finnish sites: in a boreal forest site in Hyytiälä and in an urban site in Helsinki. In both sites the measurement period covered almost a whole year and thus the seasonal variation of sub-3 nm particle concentration can be investigated.

METHODS

In Hyytiälä the measurements were performed at the SMEAR II (Station for measuring Forest-Ecosystem-Atmosphere relations) station inside a rather homogeneous Scots pine forest (Hari and Kulmala, 2005). In Helsinki the measurements were conducted at the SMEAR III station (Järvi et al., 2009), which is located in the university campus area and surrounded by parking lots, university buildings and deciduous forest. The measurements took place during 8 May 2015 – 30 April 2016 in Hyytiälä and during 8 January – 31 December 2015 in Helsinki.

In both measurement sites the size distribution of particles between 1 and 2 nm was measured with a PSM (Airmodus A11), which is a mixing-type CPC using diethylene-glycol as a working fluid (Vanhanen et al., 2011). In addition, the particle size distribution between 3 and 1000 nm was measured with a twin-DMPS (Differential Mobility Particle Sizer) system (Aalto et al., 2001). By combining PSM and DMPS measurements, the concentration of particles between 1 and 3 nm in four size bins (1.1–1.3 nm, 1.3–1.5 nm, 1.5–2.0 nm, and 2.0–3.0 nm) was obtained.

RESULTS

The median particle concentrations in different sub-3 nm size bins in Hyytiälä and Helsinki are shown in Table 1 for different seasons. In Hyytiälä the total sub-3 nm particle concentration was highest during summer and lowest in winter. This indicates that organic compounds, originating from the vegetation, likely participate in the formation of sub-3 nm particles in boreal forest. When studying particle concentration separately in different sub-3 nm size bins, the summer-time maximum can be observed to be most pronounced in the smallest size bin (1.1–1.3 nm). Thus, organic vapors may be important precursors especially for the smallest clusters. On the other hand, in the largest size bin (2.0–3.0 nm), the particle
concentration was highest in spring, which implies that at that time of year the conditions in Hyytiälä are most suitable for the initial growth of particles. This is consistent with the previous observations on the high frequency of new particle formation events in Hyytiälä during spring (Dal Maso et al., 2005).

In Helsinki the concentration of sub-3 nm particles was higher than in Hyytiälä and did not exhibit a similar seasonal cycle. The sub-3 nm particle concentration was highest in spring and winter and lowest in summer and autumn. High sub-3 nm particle concentrations detected in winter suggest that in Helsinki anthropogenic sources of precursor vapors are probably more important than biogenic sources.

CONCLUSIONS

The seasonal variation of 1–3 nm particle concentration was investigated based on PSM measurements at two Finnish sites. In a boreal forest site in Hyytiälä the concentration of sub-3 nm particles was observed to be highest in summer and lowest in winter, which indicates that organic vapors originating from the vegetation are likely important for their formation. In an urban site in Helsinki the sub-3 nm particle concentration was found to be high also in winter, which suggest the importance of anthropogenic sources of precursor vapors.

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<table>
<thead>
<tr>
<th>Measurement site</th>
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<tr>
<td></td>
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<td>HEL aut</td>
<td>1134</td>
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<tr>
<td>HEL wint</td>
<td>2059</td>
</tr>
</tbody>
</table>

Table 1. Medians of sub-3 nm particle concentration in different size bins in Hyytiälä (HTL) and in Helsinki (HEL). Data are divided into different seasons: spring (spr), summer (sum), autumn (aut), and winter (wint).
REFERENCES


EFFECT OF ATMOSPHERIC OXIDATION TO ICE NUCLEATION CAPABILITIES OF VEHICULAR AND COMBUSTION EMISSIONS

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Keywords: ICE NUCLEATION, SPIN, ATMOSPHERIC AGING, COMBUSTION EMISSIONS.

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.

The IN efficiencies of combustion emissions from firewood burning and vehicular emissions from 95E10 fuel were studied using a commercial ice nuclei counter SPIN, which uses continuous flow diffusion chamber technique. The experimented temperature regime was cirrus-relevant, from 233 K down to 224 K and studied samples included primary emissions from both sources and secondary emissions from 95E10.

EXPERIMENTS AND RESULTS

Vehicular emissions were studied in the Ilmari aerosol chamber facility, for which a detailed description can be found by Leskinen \textit{et al.} (2015). Emissions were generated from a vehicle on a dynamometer and the driving cycle was repeated on constant settings. The test vehicle was a EURO7 compliant Volkswagen Golf 1.2 FSI equipped with a direct-injection petrol engine. The test fuel used was EN228 compliant 95E10 petrol-ethanol mixture which is commonly available in Finland and Central Europe. Primary emissions were measured during the car operation. The IN activity of secondary emissions formed from photolysis of vehicle emissions in atmospheric simulation chamber were also measured. In aging experiments, primary emissions and gaseous compounds were oxidated in a flow-through reactor PEAR prior to ejection into the aerosol chamber. The PEAR is equipped with adjustable UV lights enabling OH exposure corresponding to several days in the atmosphere.

The results indicate that both primary and secondary (SOA, Secondary Organic Aerosol) emissions from 95E10 fuel are not efficient ice nuclei in deposition mode, as Figure 1 shows. Comparison to heterogeneous freezing line by Koop \textit{et al.} (2000) shows that homogeneous freezing is still the dominant ice formation mechanism despite of the presence of experimented samples, because the observed onset values generally require higher $RH_{\text{ice}}$ than homogeneous freezing predicted by the parameterization. Atmospheric oxidation due to aging was not observed to have a distinguishable effect of IN efficiency; this may be due to initially high oxidation of combustion PM and further oxidation does not change the IN efficiency. Also external mixing with α-pinene did not result in differences that are greater the instrument uncertainty. For fresh exhaust gas all observations below water saturation (blue line in Figure 1) for 2 \% ice activation were...
between 147 % and 156 % RH, which agrees with results for soot presented by Hoose and Möhler (2012) in their review article. The results are also close to ones by Kulkarni et al. (2016) for diesel soot particles.

Figure 1. 2 % activated fraction onset values of typical particle sizes of fresh exhaust gas, fresh and aged exhaust gas SOA and the contribution of external mixing with α-pinene. The solid blue and dashed black lines represent water saturation and homogeneous freezing line by Koop et al. (2000) for 60 nm particles, respectively. Error bars represent the maximum effect of instrument uncertainty to RH_{ice} during the experiment when onset was observed.

Wood combustion experiments were carried out using the SPIN at same temperature range than the above presented experiments while emissions were generated from two types of firewood, spruce and beech. Primary emissions were aged in the PEAR to different corresponding atmospheric ages. Two commercially available heaters, a Tulikivi model Hiisi-5 and an Aduro model 9-3, were used. The observations were collected during the flaming phase of burning via starting each experiment 5 minutes after ignition of wood batch and ending it before the smouldering phase. The results are presented in Figure 2.
We found that atmospheric oxidation has only small effect on IN capability of wood combustion particles, the observed differences were within the instrument uncertainty boundaries. Comparison to heterogeneous freezing line by Koop et al. (2000) shows again that wood combustion emissions are not efficient ice nuclei in deposition mode at this temperature range. All 2 % activation onsets were between 149 % and 154 % RH_{ice}, which corresponds well to earlier experiments presented by Hoose and Möhler (2012) in their review article.

**SUMMARY AND CONCLUSIONS**

The IN capabilities of emissions from a direct-injection engine and two heaters were studied using a commercial ice nuclei counter SPIN for different atmospheric ages. To our knowledge these were the first IN experiments on emissions from a modern direct-injection engine and 95E10 fuel. The results show that primary emission, i.e. fresh exhaust gas, has a similar IN efficiency than what is reported in literature for soot and diesel exhaust. Atmospheric oxidation does not appear to have an effect on IN efficiencies from primary and secondary (SOA) emissions, which may be due to high initial oxidation in the combustion process. Addition of α-pinene via external mixing may have an effect on IN efficiency but the observed one was within the uncertainty of the instrument. Although experimented emissions were inefficient ice nuclei below water saturation, they still may contribute to formation of liquid water which then freezes homogeneously.

The results from wood combustion experiments agree with literature values for fresh emission, but aging does not appear to have an effect on their IN efficiency. Therefore, together with vehicular experiments, it can be concluded that atmospheric oxidation through aging does not change the IN efficiencies of PM emissions from experimented combustion processes.

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INTRODUCTION

The most common method of forest management in Finland is rotation forestry including clearcutting and forest regeneration. Typical clearcutting involves removing stem wood and leaving logging residues (foliage, branches, and roots) on the site. This changes the site’s microclimate, vegetation structure and respiring and photosynthesizing biomass, which may affect the carbon balance of the site (e.g. Jandl et al., 2007). Also, the logging residue above and belowground is known to have an enhancing effect on carbon dioxide (CO\textsubscript{2}) and nitrogen oxide (N\textsubscript{2}O) emissions, but methane (CH\textsubscript{4}) emissions stay the same (Mäkiranta et al., 2012). On the other hand, the ground vegetation recovers rather quickly after logging at drained peatlands (Mäkiranta et al., 2010) and also at mineral soil sites (Palviainen et al., 2005).

In forestry-drained peatlands, the summertime water table level (WTL) and tree biomass correlate (Sarkkola et al., 2010). Therefore, after clearcutting, the WTL should rise due to increased throughfall and decreased transpiration of trees. Due to the risen WTL, the thickness of the oxic peat layer decreases, and following that the peat composition rate and CO\textsubscript{2} emissions decrease (e.g. Turetsky and Louis, 2006). On the other hand, the CH\textsubscript{4} oxidation by methanotrophs, i.e. the bacteria consuming CH\textsubscript{4}, in the soil is diminished, while the conditions for methane producing bacteria will be more favorable, which together have an increasing impact on the emissions of CH\textsubscript{4} to the atmosphere (e.g. Roulet et al., 1992).

Here our aim was to study whether the environmental impacts of peatland forestry can be reduced by moderately rising the WTL, which should eventually decrease the CO\textsubscript{2} emissions, but not to switch the site from a CH\textsubscript{4} sink into a source. N\textsubscript{2}O emissions are expected to increase due to the logging residues.

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. After that, the tree stand was a mixture of Scots pine, Norway spruce and Downy birch.

To achieve a moderate (about 20 cm) rise in the water level from the original –50 cm level, we conducted a partial cutting of the tree stand in our study site in spring 2016 with all pine trees, comprising ca. 75 % of the tree biomass, being removed in the harvest operation. The dense spruce understory was left to regenerate the tree stand. We also established a control plot which was left in the original state and a clear-cut plot where the whole tree stand was cut down to compare the impact of different management practices.
The effect of timber harvesting and the moderate water-level rise on CO₂ fluxes, energy fluxes and evapotranspiration were studied with the eddy covariance method before (2009–2015) and after (2016–) the harvest. Also, at each plot, there was a weather station monitoring incoming and outgoing radiation and temperature and moisture in the air and soil. WTL was monitored from over 40 wells around the site with automatic loggers and manual measurements. In addition, aquatic inorganic and organic carbon and nitrogen losses were monitored with manual and automatic sampling. The greenhouse gas (GHG) fluxes at the forest floor were measured with six automatic chambers at both the partial harvest and the control plots throughout the year. The chambers closed hourly and the sample gas was sucked into a cavity ring-down spectroscopy analyzer (Picarro Inc, Santa Clara, CA, USA) and analyzed for CO₂, CH₄ and water vapor concentration with 5 second time resolution. In addition, at the partial harvest plot, the chamber system also included a gas analyzer (Los Gatos Research, San Jose, CA, USA) measuring the N₂O and carbon monoxide fluxes with the Off-axis ICOS technology. At the control plot, due to lack of a stationary gas analyzer, N₂O fluxes were measured from separate sampling lines (8 measurement points) either by the syringe sampling or by using portable gas analyzer (Gasmet Technologies Oy, Helsinki, Finland) every two weeks. The same measurement method was applied at the clear-cut plot, but all the gases were measured with the portable gas analyzer. These chamber measurements did not include any logging residue, however, we have set up several logging residue points at the partial harvest and clear-cut plots to quantify the effect of the logging residue on the GHG balance, but the results are not shown here.

RESULTS

The WTL rose after the harvest at both the partial harvest and clear-cut sites. During the first summer of 2016, the rise in WTL has been ~30 cm at the clear-cut plot and ~10 cm at the harvest plot (Figure 1).

The qualitative analysis of CO₂ flux measurements made with the eddy covariance technique at the partial harvest plot showed about 50 % decrease in the daytime sink (Figure 2). We have not analyzed the quantitative changes in nighttime respiration yet, but it seems that there was no significant change in the ecosystem respiration. This would indicate decrease in the net uptake of CO₂ or increase in the net CO₂ emission as compared to situation before the harvest. This was expected, since the spruce canopy is still recovering from the harvest and cannot yet compensate the uptake by the harvested pines. On the other hand, the total respiration has not probably decreased due to the logging residues left to decompose at the site.

The flux measurements with automatic and manual chambers at the forest floor did not show any noticeable difference between the partial harvest and the control plots in CO₂ and CH₄ fluxes (Figure 3). However, at the partial harvest plot, the N₂O emissions seem to have increased after the harvest. In the case of clear-cut plot, the CO₂ fluxes have not changed compared to the partial harvest and control plots. On the other hand, the clear-cut site has turned from a CH₄ sink to a source. In addition, before the harvest, the clear-cut site was N₂O neutral but now it is a significant N₂O source.

CONCLUSIONS

The WTL at the clear-cut site has risen the most, which was expected as there is no transpiration from the trees anymore, and even ground vegetation was mostly destroyed. We could also see some rise in WTL at the partial harvest site as a result of the harvest. The decrease of daytime sink measured by the eddy covariance at the partial harvest site was also expected, since the spruce canopy is still recovering from the harvest and cannot yet compensate the uptake by the harvested pines. On the other hand, the total respiration has not probably decreased due to the logging residues left at the site. In the case of the chamber measurements, more detailed analysis is needed to see if there is some significant difference in CO₂ fluxes between the plots, because the rise in WTL is expected to decrease the peat decomposition rate and thus the CO₂ emissions. Also, the rise in the WTL at the clear-cut plot was large enough to turn the plot from CH₄ sink to a source by decreasing the thickness of the oxic layer, but the rise in the WTL at the
partial harvest site seemed not to affect the CH$_4$ fluxes there. The increase in N$_2$O emissions at the partial harvest and clear-cut sites can be explained with the decomposition of below-ground residues as there is no above ground residues on the surface the chambers are measuring.

![Figure 1](image1.png)

**Figure 1.** Water table level measured from one point from sampling lines at partial harvest (black), control (green) and clear-cut (cyan) plots. The error bars on the partial harvest curve shows the 95% confidence interval. The red vertical bar indicates the time of the harvest.

![Figure 2](image2.png)

**Figure 2.** Time series of the half-hourly CO$_2$ flux measured with the eddy covariance technique from the partial harvest area in the last six and half years. The red vertical bar indicates the time of the harvest.
Figure 3. Daily mean flux of CO$_2$ (upper panel), CH$_4$ (middle panel) and N$_2$O (bottom panel) measured with automatic and manual chambers at the forest floor at partial harvest (blue), control (green) and clear-cut (red) plots. The red vertical bar indicates the time of the harvest.

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COUPLING OF THE SOA SCHEME VBS-SALSA TO THE CHEMISTRY MODULE MOZ IN ECHAM-HAMMOZ

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Keywords: CLIMATE MODELLING, SECONDARY ORGANIC AEROSOL.

INTRODUCTION

Secondary organic aerosol (SOA) is an important contributor to the total atmospheric aerosol mass. The chemical and physical processes leading to SOA formation in the atmosphere are very complex and thus hard to model in detail in global climate models. A successful method to simulate SOA formation is to use a volatility basis set (VBS) [Donahue 2006], which describes the gas-to-particle partitioning of semi- and low-volatile organics by grouping them into volatility groups. In global models, however, it is also important to resolve the chemistry of the oxidation of volatile organic compounds (VOC) to SOA-forming species well enough. Here we couple the semi-explicit chemistry solver MOZ to the aerosol module VBS-SALSA and model SOA production for SOA-forming species of isoprene oxidation.

METHODS

We use the global aerosol-climate model ECHAM-HAMMOZ (ECHAM6.3-HAM2.2-MOZ1.0) for our simulations, which is a combination of the sixth generation atmospheric circulation model ECHAM6 [Stevens 2015], the aerosol module HAM and the semi-explicit chemistry solver MOZ. HAM describes aerosol emissions, transport, removal, chemistry, and radiative properties [Stier 2005]. In the sectional aerosol microphysical model SALSA, aerosol distributions are discretized using 10 size bins with average particle diameters ranging from 3 nm to 10 μm [Kokkola 2008]. In its basic setup, SALSA includes the chemical species sulphate, (non-volatile) organic carbon, black carbon, sea salt, and mineral dust. MOZ is derived from the chemistry solver MOZART-3 [Kinnison 2007], with 250 species and 700 reactions. It produces SOA precursors from isoprene and monoterpenes. Biogenic VOC emissions are modelled using MEGAN2.1 [Guenther 2012].

To model the SOA production from isoprene oxidation, we modified the existing VBS-SALSA scheme such that all SOA-forming species are implemented explicitly within the VBS framework. This enables us to also treat the evaporation of semi-volatile compounds back into the gas phase correctly, which allows for further treatment in MOZ. The species that are included into the VBS mechanism are chosen based on a pre-analysis of the volatility of all notable oxidation products of isoprene. The criterion for selection was a maximum vapour pressure, p₀, of 10⁻⁷ atm at 298 K. The included species are called C₅₉OOH (p₀=1.0x10⁻⁴ at 298 K), LNISOOH (p₀=2.18x10⁻³ at 298 K), LC₅₇₈OOH (p₀=2.01x10⁻⁴ at 298 K), and LISPOOHOOH (p₀=3.83x10⁻⁷ at 298 K) and are products that result from different reaction pathways. The temperature dependence of the vapour pressures follows the Clausius-Clapeyron relation.
RESULTS

Figure 1 shows preliminary results of the SOA burden that results solely from the atmospheric oxidation of isoprene. In low latitudes SOA aerosol burden is substantial both in absolute and relative terms. Especially in mid-latitudes we see a clear improvement in model performance compared to using the very simple pseudo-chemistry of the uncoupled VBS-SALSA.

![Figure 1](image)

Figure 1. Yearly average burdens of particulate SOA-forming species that are formed through isoprene oxidation in the atmosphere.

CONCLUSIONS

We have successfully coupled the SOA module (VBS-SALSA) to the semi-explicit chemistry module MOZ in ECHAM-HAMMOZ. The results are still preliminary, but research using this new model is currently under way.

ACKNOWLEDGEMENTS

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FOUR YEARS OF CO₂ EXCHANGE MEASUREMENTS REVIEL THAT THE ECOSYSTEM SCALE FLUXES ARE STRONGLY TEMPERATURE-LIMITED IN A SUBARCTIC SCOTS PINE STAND, SMEARI

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INTRODUCTION

Northern boreal forests experience cold and snowy winters, short growing seasons and low but sufficient annual precipitation. Most of the carbon in northern boreal forests is stored in soils with slow decomposition rates due to low soil temperatures and recalcitrant compounds (Hobbie et al., 2000). Due to the slow decomposition, boreal forests are known as carbon sinks (Fan et al., 1998) but the magnitude and the factors that control this sink are still unclear.

The sink-limitation hypothesis (Körner, 2003) states that in high latitudes, tree growth is regulated by temperature which controls the activity of growing meristems, while photosynthetic production together with carbon storages are always sufficient to maintain the growth. Leuzinger et al. (2013) showed support to the hypothesis by demonstrating in a modelling study that the annual tree growth was more clearly related to accumulated temperature than to accumulated photosynthetic production in high latitudes. Several studies have shown that the radial growth, for example, of the northernmost conifers is promoted by warm temperatures in spring (e.g. Babst et al., 2012; Henttonen et al., 2014) and in summer (Korpela et al., 2011; Seo et al., 2011; Xu et al., 2014). Still, all currently available dynamic global vegetation models simulate plant growth via source-limited processes.

The aim of this study was to test if temperature drives the annual variation in the net CO₂ exchange (NEE) of a subarctic Scots pine stand and whether the variation in the carbon fluxes can explain the observed growth variation. In addition, the goal is to arrive at a more reliable estimate how trees and the forest carbon sink in such forests might behave in future.

METHODS

The Värriö Subarctic Research Station (67°46′N, 29°35′E) is located below the current northern altitudinal treeline in north-eastern Finnish Lapland. The mean annual temperature for the climatological normal period (years 1971–2000) was −0.9 °C, mean annual precipitation 592 mm, and the length of the growing season 114 days (Pirinen et al., 2012).

CO₂ fluxes were measured at the nearby Station for Measuring Ecosystem-Atmosphere Relations (SMEAR I). It is located on the summit plateau of Kotovaara dominated by Scots pines with an average height of 8.6 m and an average diameter of 13.9 cm. The fell was naturally populated consisting of young
and old trees of various age with a density of approx. 750 trees ha\(^{-1}\). The ground vegetation is comprised of a variety of mosses, lichen and dwarf shrubs such as *Vaccinium myrtillus*, *Empetrum nigrum*, *V. vitis-idaea* and *Calluna vulgaris*.

Air humidity and temperature were measured at 2 m height at SMEARI. Photosynthetically active radiation (PAR) was measured above the canopy. Soil temperature was measured near EC tower in 2 cm depth in the organic layer. Soil volumetric water content was measured in the uppermost 5 cm. Temperature sum was calculated with 5 degree threshold. The daily average temperature occasionally dropped below 5 °C during the growing season but we did not re-zero the sum at these points as long as the daily minimum temperatures remained above 0 °C.

Precipitation (rain and snow) were measured at the Salla Värriötunturi weather station, managed by the Finnish Meteorological Institute and located at the Värriö Research station. Also the first snow was detected by this station. Snow depth was measured at a landscape-level along a 2-km long transect with 60 permanent observation poles across the Värriö fell in the north-south direction. The setup is described in more detail by Kivinen and Rasmus (2015). Since the SMEARI site is more open than the area around the research station, we avoided using these snow records at the weather station but estimated the time of snowmelt at SMEARI from soil temperature measurements. We assumed that the snow thawed when the soil temperatures rose above 0.3 °C.

The eddy covariance (EC) system was installed 5 m above the forest canopy in 2012. The flux calculations, gapfilling of NEE, and partitioning it to gross primary production (GPP) and total ecosystem exchange (TER) were performed mainly as in Kolari et al. (2009).

We utilized trees that were broken during the heavy snow in winter 2015–2016 to determine the annual growth of shoots. The annual height increments were measured from 9 main shoots and as many lateral shoots in the upper canopy. In addition, the lengths were measured from six fallen branches from the upper canopy. The needle lengths were determined from three needles selected from those same shoots resulting in 27 needle lengths for the main shoot and 45 needle lengths for the lateral shoots. The annual height increment of the dwarf shrubs were determined systematically on a 45-meter long transect where we measured the increment of the three closest individuals of *Vaccinium vitis-idaea*, *V. myrtillus* and *Empetrum nigrum* at three metre intervals resulting in 45 individual length increments for each species.

**RESULTS**

The weather conditions differed greatly during the campaign years.2012–2015 The growing season 2013 was the warmest, sunniest and driest having the highest mean temperature and PAR and the lowest precipitation and mean RH. Growing season 2015, on the other hand, was the chilliest and moistest having the lowest temperature and PAR together with the highest precipitation and mean RH. The other years fall somewhere between these two extremes: 2012 was a chilly and 2014 a warm year both having intermediate mean PAR, RH and precipitation.

According to EC measurements, daily NEE was positive i.e. the forest was a source of carbon during the off-seasons transforming into a carbon sink around mid-May (Fig. 1A). In the autumn, daily NEE turned positive usually in early September. Daily NEE was sometimes positive during the active season mainly on rainy days accompanied with low radiation. All years resulted in negative annual NEE i.e. the stand acted as a carbon sink during the campaign years (Fig. 1D). NEE was closest to zero in the chilliest year 2015 (-5 g C m\(^{-2}\) yr\(^{-1}\)) and most negative in the warm year 2013 (-26 g C m\(^{-2}\) yr\(^{-1}\)). However, 2012 resulted in more negative NEE than 2014 even if that summer was slightly chillier. The warm and sunny year 2013 had the highest annual GPP (190 g C m\(^{-2}\) yr\(^{-1}\), Fig. 1F) whereas the lowest annual production resulted from the chilly and rainy year 2012 (148 g C m\(^{-2}\) yr\(^{-1}\)). TER followed the same order with the highest annual respiration in 2013 (165 g C m\(^{-2}\) yr\(^{-1}\)) and the lowest in 2015 (143 g C m\(^{-2}\) yr\(^{-1}\), Fig. 1E).
GPP and TER showed positive correlations with temperature sum accumulated until the end of August with $R^2$ values of 0.88 and 1.00, respectively (not shown). There was a negative correlation between annual NEE and temperature sum but the $R^2$ was poor (0.45). For example, the $R^2$ value between NEE and precipitation in May-Aug was higher (0.96).

In average, there were small but statistically significant differences in the final shoot lengths in Scots pines and dwarf shrubs. In 2015, the growth was significantly lower in Scots pine needles, and in the stem of *Vaccinium myrtillus* and *Empetrum nigrum* compared with the other years. *Vaccinium vitis-idaea* did not show any notable annual variation in its stem growth during the campaign years. The final lengths were difficult to connect with the variation in the annual weather characteristics or CO$_2$ fluxes except for Scots pine needles that had large annual variation in the mean needle length, mainly correlated with the temperature sum.

![Figure 1](image_url)

Figure 1. Daily (A-C) and cumulative (D-F) NEE, TER and GPP measured above the canopy in 2012–2015. X-axes represent the day of year (1–365). For clarity, the daily rates are moving averages over 7 days.
CONCLUSIONS

The studied Scots pine ecosystem at the Northern timberline showed notable year-to-year variation in the sink strength. TER and GPP were positively connected to temperature sum indicating clear temperature-limitation of those processes. Thus, the study supports assumptions on increased CO$_2$ uptake and ecosystem respiration with increasing temperatures. However, the growth variation did not clearly follow the variation in GPP or NEE that might be a signal of sink-limitation of tree growth at these ecosystems but the sink-source dynamics of these plants still need further studies.

ACKNOWLEDGEMENTS

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REFERENCES


ASSESSING THE IMPACT OF CITY PLANNING ON POLLUTANT VENTILATION USING A LARGE-EDDY SIMULATION

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Keywords: large-eddy simulation, pollutant ventilation, air quality, urban planning

INTRODUCTION

Ventilation and dispersion of traffic-related air pollutants inside street canyons and courtyards were studied using four alternative city-block-design versions. The study employed a large-eddy simulation (LES) model with embedded Lagrangian stochastic particle and canopy models to simulate transport of pollutants and the aerodynamic impact of trees on pollutant transport, respectively. Here transport of pollutants refers to the transport of massless air parcels corresponding to passive scalars. Understanding the mechanisms behind pollutant transport and maximizing ventilation of street canyons and courtyards by choosing the optimal city-block-design is essential for ensuring a good air quality in densely built neighbourhoods. Hence, the aim of the work was to rank the alternative city-block-design versions according to their capability to transport traffic-related pollutants away from the pedestrian level, and this way provide urban planners and decision makers vital information on the impact of urban morphology on street canyon ventilation.

METHODS

The turbulent wind field and pollutant transport over an urban surface were simulated using a LES model PALM (Maronga et al., 2015) coupled with a Lagrangian stochastic (LS) particle model. Furthermore, the aerodynamic impact of street trees and a surrounding forest on pollutant transport was included by means of an embedded plant canopy model. The embedded models were revised in the study to take into account the horizontal heterogeneity of the particle sources (streets) and vegetation canopy.

The numerical simulations using the PALM-LS model were conducted using four different city-block-design versions with a varying orientation, height and shape of the buildings. Furthermore, street trees (Tilia) as well as a surrounding forest area was included in all versions in order to make the simulations more realistic. The information on the surface elevation and buildings, pollutant sources and tree canopy were fed to the model as two-dimensional ASCII-formatted raster files.

In this study, three-dimensional two-way self-nesting (Hellsten et al., 2016) was applied for the first time in PALM. Nesting enables to have both a large computational domain and a high enough resolution in the main area of interest without making the simulation computationally too expensive. In the simulations, a "child" computational domain with a grid spacing of 1 m and dimensions of 2048 m × 1024 m × 96 m or 1536 m × 1536 m × 96 m, depending on the applied meteorological conditions, was defined inside the "parent" computational domain of 4096 m × 2048 m × 384 m with a grid spacing of 2 m. PALM was run in parallel in both domains with respective computational set-ups, and the domains communicated at their common boundaries. The particle model was run only inside the child domain.

Two contrasting meteorological conditions with neutral and stable atmospheric stratification and south-western and eastern wind direction, respectively, were applied in order to rule in the relative impact of
weather conditions on pollutant transport. The simulations were performed over a time period of 66 minutes.

Ventilation and dispersion capacities of the different city-block-design versions were assessed by analysing the temporal means of the three following measures: the particle concentration ($pc$), the turbulent vertical particle flux ($F_p$) and the particle dilution rate ($D$). A suggestive ranking of the versions was performed by calculating the horizontal mean values of these temporal mean values separately for the boulevard, the other street canyons, the courtyards and the surroundings, and rating the performance of each version based on each analysis measure on a relative scale 0-1.

CONCLUSIONS

All analysed measures showed strong dependence on both the urban morphology and meteorological conditions. Varying building height and shape as well as the length of the canyon modified the accumulation of $pc$ inside street canyons and thus also $F_p$ above them. Despite the vicinity of the particle sources, the courtyards remained relatively clean. In spite of equal particle release rates, clear differences in $F_p$ between the different design versions could be observed. $D$ was governed by the horizontal advection and thus was related to the volume of street canyons parallel to the wind direction. $F_p$ measures only turbulent transport whereas $D$ includes the advective transport as well, which explains the differences between these two measures.

Focusing on the street canyons, where the concentration levels are highest, the applied ranking suggested that the city-block-design version with a varying roof height and short street canyons would be the best option to build the city blocks regarding the ventilation capacity. This was especially pronounced in meteorological conditions with stable stratification and eastern wind direction. Previous studies on the impact of roof height variability on the ventilation of street canyons supported the results.

This was the first high-resolution LES study conducted over a real urban topography applying sophisticated measures to assess pollutant dispersion and ventilation inside street canyons and courtyards. The numerical methods employed in PALM are novel and highly developed. The results of the study can directly be applied when planning new pleasant neighbourhoods in an urban environment.

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REFERENCES


INTRODUCTION

Atmospheric heavy metals have 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 and source apportionment of twelve (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) heavy metals in particulate matter (PM10).

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. The heavy metal (HM) PM10 samples were collected weekly on Teflon filters, digested in the laboratory and analyzed with ICP-MS. The trend analysis 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). The positive matrix factorization (PMF) method was applied in source apportionment for weekly HM data combined with other pollutant data. The PMF method is described elsewhere (Paatero and Tapper, 1994; Paatero, 1997).

CONCLUSIONS

The atmospheric concentrations of heavy metals at Pallas are rather low compared to other European sites. This is due to minor domestic emissions in the sub-arctic area and long distance to the large European source areas. In Figure 1, the measured and modelled atmospheric PM10 concentrations with annual trends are shown for arsenic, cadmium, nickel and lead. These are the four trace elements the EU member countries are obliged to monitor according to the European legislation. The annual concentrations were from the lowest values to highest Co<Cd<<Cr<As<Mn<Cu, Ni, V<Pb<Zn<<Al<Fe. The seasonality of the elements varies. Some elements, e.g. As, Cd, Pb, V and Zn have strong seasonality with peaks in the late winter due to the higher amount of energy production. For elements of significant soil dust origin, e.g. Al, Fe and Mn, the highest concentrations are observed during the spring and early summer after snow melt due to re-suspension.

The trend analysis showed that most of the elements are decreasing 2-3 % per year. These decreases are substantial resulting in decreases of 34-55 % during the whole measurement period. Only chromium and zinc did not have statistically significant trends. The reductions are due to the emission reductions in Finland and broader in Europe. Additionally, the high As, Ni and Cu emissions from the metallurgical industry in Kola Peninsula (about 300 km from Pallas) have previously been connected to elevated deposition at the site (Kyllönen et al., 2009). There is no official emission records available for the smelters but our results indicate the emissions have possibly been reduced. Our results give evidence that the emission reductions have had a positive impact on the air quality.
Additionally, we repeated the trend analysis for a shorter time series of 10 years (2006-2015) to see whether the decrease is still taking place during the recent years. During that time period, most of the heavy metals (Cd, Co, Fe, Mn, Ni, Pb, V, Zn) were decreasing at a rate of 4-6 % per year. No statistically significant trend was found for Al, As, Cr and Cu.

Figure 1. Atmospheric measured and modelled concentrations (in ng m$^{-3}$) with annual trends of arsenic, cadmium, nickel and lead at Pallas in 1996-2014. The trends are significant at the 99 % confidence level (**).

The sources of the HMs were investigated by means of trajectory analyses and the multivariate statistical method PMF. A selection of parallel measurements of inorganic gases and chemically speciated aerosols were used as supportive material. The five factors were identified as soil, background, Kola industry, long-range transported (LRT) episodic particles and LRT neutralized secondary particles (Fig. 2). Soil was the major source of Al, Fe and Mn while Hg was mostly in the background factor. Three different industrialized sources were identified with Kola industry being the major source of Cu, Ni, As and Co. The remaining Cd, Cr, Pb, V, and Zn were mostly found in the seasonal (episodic) and non-seasonal (neutralized) LRT factor.
Figure 2. The factor compositions as a percentage of each component loaded into each respective factor (left), and the relative source contribution time series (right).

REFERENCES


INTRODUCTION

Forest fires are one of the most important natural disturbances in boreal forests that strongly influence the carbon dynamics - reducing the total carbon storage and shifting ecosystem carbon pools from living biomass to necromass (Sullivan et al., 2011). As an immediate effect of fire, a pulse of CO$_2$ is released to the atmosphere through the combustion. In the long run fire disturbances also affect the CO$_2$ fluxes originating from the decomposition and root and rhizosphere respiration (Hart et al., 2005).

Different studies have found contradictory results on the length of post-fire effect on soil CO$_2$ effluxes, as different fires are with different severity and they occur in different ecosystems with different ecosystem properties. Kulamala et al., (2014) found that in the prescribed burning site in boreal forest the reducing effect of fire on CO$_2$ efflux lasts only couple of years. Köster et al., (2015) reported that in the northern boreal forest with low intensity fire the effect can be around five years. But there are also studies that have reported that the effect of fire on CO$_2$ efflux can last more than decade (Sullivan et al., 2011).

Here we assessed the changes occurring in soil CO$_2$ efflux within seven years after fire disturbance in natural northern boreal subarctic Scots pine (Pinus sylvestris L.) forest.

METHODS

Measurements were conducted in natural northern boreal subarctic coniferous forests located in the Värriö Nature Reserve (67°46’ N, 29°35’ E) in Finnish Lapland. The sampling sites were situated north of the Arctic Circle, close to the northern timberline at an average altitude of 300 m above sea level. The Värriö Nature Reserve lowlands are covered by taiga, where the main tree species is Scots pine. The soil in the area is classified as haplic podzol (Köster et al., 2014). We used two different fire areas in this study – fire in a year 2009 and fire in a year 1859 (control area where the effects of fires are expected to be over).

Soil CO$_2$ efflux measurements were performed on twelve permanent measurement collars (diameter 22 cm) at each fire area in years 2011 – 2016. The measurements were performed four to six times through growing season (June - September). The permanent collars were sealed with sand and placed randomly (at least 3 m apart from each other) through the fire area. Soil CO$_2$ efflux was measured using a dark portable cylindrical respiration chamber (0.24 m in height and 0.22 m in diameter). Soil CO$_2$ efflux in our study was defined as the sum of respiration by soil microorganisms, mesofauna, macrofauna and plant roots. The CO$_2$ concentration was recorded over the 5-minute chamber deployment time with a diffusion type
CO₂ probe (GMP343, Vaisala Oyj, Vantaa, Finland) and the air humidity and temperature in the chamber was measured using a relative humidity and temperature sensor (HM70, Vaisala Oyj, Vantaa, Finland).

RESULTS AND CONCLUSIONS

We found seasonal trends in CO₂ effluxes from fire damaged areas through all the years. There was increasing trend of CO₂ effluxes towards the end of the summer, as the fluxes were lowest in June and increased through growing season, and were highest in August. If the average CO₂ effluxes of newly burned (fire in year 2009) and control (last fire in 1859) areas were compared, we found significant differences between the areas measured in years 2011 and 2012. Measurements from year 2013 showed that in June and July we had a significant difference between the areas, but in August there was no difference between the compared areas. We think that one reason here can be the low amount of precipitation, as the year 2013 was extremely dry. The measurements from year 2014 showed clear difference between the areas. The measurements from years 2015 and 2016 showed no significant difference between the areas in June and July, but there was significant difference between the areas if the measurements from August were compared, as the CO₂ efflux was significantly higher in control areas at that time. Such results can be explained by rather quick recovery of ground vegetation and germination of new tree seedlings, resulting in an increase in root and rhizosphere respiration, which appears to compensate the decrease of CO₂ efflux originating from decomposition processes.

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Increasing midlatitude cooling by seasonally changing sulfur injections

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Keywords: Solar Radiation Management, Climate Modelling, Sulfate aerosols, Radiative forcing.

INTRODUCTION

Solar radiation management (SRM) by injecting sulfur to the stratosphere has been shown to have potential to counteract global warming. In the future, such a method may be considered as an option for slowing down global warming, if reducing of greenhouse gases (GHG) has not been achieved fast and effectively enough. Sulfur is suggested to be injected as SO\textsubscript{2} which oxidizes to sulfate particles. Particles would reflect solar radiation back to space which would lead to cooler climate. Many of the previous studies propose injection to the equator where solar intensity is averagely highest and from where sulfur would spread evenly to the both hemispheres. This has been thought to be the most effective injection strategy. However sulfate particles would reflect the incoming solar radiation (SW) while increased GHG concentration would absorb the outgoing longwave (LW) radiation. Difference in the intensity of the radiation between low and high latitudes is larger for SW radiation than LW radiation. Thus compensating global mean change in LW radiation by altering SW radiation would generally lead to situation where low latitudes will cool and high latitudes will warm even thought the global mean temperature would remain at the same level as before. A reduced temperature gradient between low and high latitudes would has impact for example precipitation (Ferraro et al, 2014). If sulfur is injected at the equator, the cooling effect would be concentrated to low latitudes which will highlight the above-mentioned fundamental problem related to SRM. However when injecting only to the equator, in summer and winter months sulfur is not injected to the areas where solar intensity is the largest. This could be avoided by changing injection area along the seasonally changing radiation. In this case the cooling effect is concentrated relatively more to the midlatitudes and SRM could be still as effective as when injecting only to the equator. Here we study different injection strategies using two global climate models.

METHODS

In all of the simulated scenarios 5 Tg(S)/yr is injected stratosphere as SO\textsubscript{2} at the height of 20-22km and in an area ranging over a 20 degrees wide latitude band. This latitude band is changing during the year. We studied scenarios with difference phases, where the injection area is at the northern most position (from 30° N to 10° N) in June (p0), April (p2), February (p4), or December (p6). Injection areas in these scenarios are in figure 1. In addition one scenario was simulated (p2w) where 20 degrees wide injection area varies between the latitudes from 40° S to 40° N instead of 30° S to 30° N. These scenarios are compared with the scenario where sulfur is injected only to the equator (EQ).

Simulations have been performed in two steps. In the first step, we have used the aerosol-climate model ECHAM6-HAM-SALSA to define aerosol fields and radiative forcing from each of the simulated scenario. The aerosol module HAM is coupled interactively to the atmospheric model.
ECHAM6 and includes an explicit sectional aerosol microphysical scheme SALSA (Kokkola et al., 2008). SALSA calculates the microphysical processes of nucleation, condensation, coagulation and hydration describing the aerosol number and volume size distributions using 10 size sections. In the second step, simulated aerosol fields and the radiative properties are implemented to the Max-Planck-Institute’s Earth system model (MPI-ESM) (Giorgetta et al., 2013) to simulated climate effects. This implementation of radiative properties is based method used on the Laakso et al (2016), but here aerosol optical depth (AOD), single scattering albedo and assymetry factor of simulated aerosol field are implemented for 30 radiation wavelengths while in Laakso et al (2016) only aerosol effective radius and AOD at 550 nm from ECHAM-HAM-SALSA simulations and predefined look-up table was used. This new improved method would transfer the radiative properties of aerosols field from ECHAM6-HAM-SALSA to MPI-ESM more accurately than before. Our MPI-ESM simulations start from year 2010 and continue until 2100. Our base scenario follows the RCP4.5 scenario (Moss et al., 2008). All SRM scenarios follow the RCP4.5 scenario but with additional stratospheric aerosol added starting in 2020. The sulfur injections are applied for the duration of 50 years, until injections are suspended. After that we continue our simulations for 30 years.

CONCLUSIONS

As Table 1 shows, \textbf{p2}, \textbf{p4} and \textbf{p2w} lead to similar global mean radiative forcing than if sulfate is injected along the Equator (EQ). \textbf{p2} scenario was even more effective than EQ. However the difference was only 3%. It takes few months before the injected SO\textsubscript{2} is oxidized and large enough particles to reflect solar radiation has been formed. This is the reason why \textbf{p0} is not that efficient scenario, because particles have been formed after solar intensity start to decrease. On other hand in \textbf{p6} particles have already formed and they have been transported to the higher latitudes when solar intensity increases in the hemisphere. Figure 2 shows zonal mean radiative forcing in studied scenarios. \textbf{p2w} lead to relatively larger radiative forcing at the midlatitudes and smaller radiative forcing at the equator and high latitudes compared to the other scenarios.

Figure 1: Injection areas in seasonally changing injection areas in \textbf{p0}, \textbf{p2}, \textbf{p4} and \textbf{p6}
<table>
<thead>
<tr>
<th>Scenario</th>
<th>Stratospheric sulfate burden Tg(S)</th>
<th>All-sky SW forcing at TOA (W/m²)</th>
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<tr>
<td>EQ</td>
<td>6.15</td>
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</tr>
<tr>
<td>p0</td>
<td>6.15</td>
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<tr>
<td>p4</td>
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<td>-3.74</td>
</tr>
<tr>
<td>p6</td>
<td>5.98</td>
<td>-3.58</td>
</tr>
</tbody>
</table>

Table 1: Five year mean values of stratospheric sulfate burden and the global shortwave all-sky forcing.

Because there is no large change in the global mean radiative forcing between the SRM scenarios, global cooling would be similar in all of the scenarios. Injections are followed by very fast cooling and after that by slow warming after the year 2030 (fig3a). Figure 3b the shows zonal mean temperature change between years 2060-2070 compared to years between 2010-2020. As expected, low latitudes have been cooled while there is warming at midlatitudes. However there is also strong cooling especially in northern high latitudes. This is due to the our experiment setup, where SRM has been started at full force in 2020. This would lead to unrealistic cooling, increase in Arctic ice sheet and cooling feedback response compared to the years at beginning of the simulation. Overall, p2 and p2w lead to stronger cooling at midlatitudes than EQ as was expected, but also similar or even larger cooling at Tropics. This shows direct radiation changes have only a small effect on regional temperatures and seasonally changing injection would solve only part of the problem related to zonally uneven cooling effect of stratospheric sulfur geoengineering.

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Figure 3: a) Global mean temperature anomaly and b) zonal mean temperature change between years 2060-2070 and 2010-2020.

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APPLICATION OF THE ADSORPTION NUCLEATION THEORY TO DEPOSITION ICE NUCLEATION

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Keywords: Adsorption, Ice nucleation, Mineral dusts.

INTRODUCTION

Deposition ice nucleation (DIN) occurs when water vapor is nucleated directly to ice on insoluble aerosol particles at low temperatures. The traditional way to represent DIN theoretically is using the classical heterogeneous nucleation theory (CHNT), which describes the interaction between the ice nucleus and the underlying aerosol surface using a single parameter, the contact angle. Unfortunately, CHNT is not able to correctly predict the critical supersaturations at which DIN is initiated when reasonable contact angle values corresponding to measurements are used (the situation is similar with heterogeneous liquid drop nucleation, where critical supersaturations are drastically over-predicted if measured contact angles are used). Therefore, if CHNT is used e.g. in a climate model, one needs to apply contact angle values that are adjusted so that the theory matches laboratory measurements of DIN. A more recent approach is to use a purely empirical description of DIN that calculates temperature-dependent nucleation site densities based on experimental nucleation rates and aerosol surface areas. Neither the CHNT nor the nucleation site density approach is very reliable in climate modelling as one cannot be certain that they work outside the range of lab experiments for a given aerosol type. Here, we apply the recently developed adsorption nucleation theory (Laaksonen, 2015; Laaksonen and Malila, 2016) to DIN on five different mineral aerosols, and show that the theory yields predictions that are in excellent agreement with laboratory experiments.

THEORY

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

The basic idea of the new theory is to combine the multilayer Frenkel-Halsey-Hill (FHH) adsorption isotherm, and the Kelvin equation. The FHH isotherm gives adsorption layer thickness at given water vapour saturation ratio when two FHH parameters ($A$ and $B$) are known. On non-wettable surfaces, the adsorption layer is not homogeneous but consists of small droplets (Cao et al., 2011), and the Kelvin equation describes how vapour pressure is increased over the droplet surfaces compared to a flat adsorption layer. Beside the $A$ and $B$ –parameters (that describe the interaction between the substrate and the first adsorption layer, and the decay of the interaction as a function of distance in subsequent layers, respectively), the theory contains two more parameters: the contact angle $\Theta$, and the average distance between adsorption sites $s$. When $\Theta$ and $s$ are known, the sizes of adsorbed droplets can be related to the macroscopically observable adsorption layer thickness. In practice, the contact angle needs to be measured separately, and $A$, $B$, and $s$ can be obtained from adsorption measurements.
When the four parameters of the theory are known, a curve of adsorption layer thickness (or alternatively, diameter of adsorbed droplets) can be drawn as a function of water vapour saturation ratio. Because of the Kelvin effect, the curve extends to the supersaturated region, where it exhibits a maximum. Similarly as with Köhler theory of cloud drop formation, the maximum signifies the critical supersaturation for heterogeneous nucleation. Note, however, that in cases with small average distance between adsorption sites, coalescence of adsorbed droplets can initiate nucleation already at some lower supersaturation.

RESULTS

In order to apply the adsorption nucleation theory to deposition ice nucleation, we make two assumptions. The first one is that the FHH parameters determined from room temperature adsorption measurements can be applied to ice adsorption. This should be reasonable since the molecular interactions between the adsorbent surface and the adsorbed water should not depend on the phase state of the water too much (especially if the average orientation of the first adsorption layer does not change much upon freezing). The second assumption is that the contact angle of water droplets does not change when they freeze. There is experimental evidence that this is the case at least when the contact angle is close to 90° (Jung et al., 2011; Heydari et al., 2013).

Literature data for both water vapor adsorption (see Laaksonen et al., 2016, and references therein) and water contact angles (Ethington, 1990; Shang et al., 2010) was found for five different mineral dusts. These data were used as input to the adsorption nucleation theory, and critical supersaturations were calculated for sodium montmorillonite, kaolinite, illite, calcite and quartz particles. Figure 1 shows a comparison of theoretical and experimental (Eastwood et al., 2008; Welti et al., 2009) critical supersaturations. As can be seen, CHNT predicts much too high critical supersaturations, whereas the predictions of the adsorption nucleation theory are very close to the experimental results.

Figure 1. Comparison of the predictive success of adsorption nucleation and classical nucleation theories for deposition ice nucleation of water vapour on five different mineral aerosols (kaolinite 200-800 nm, montmorillonite 200-800 nm, illite 200-800 nm, quartz 1 μm, calcite 1 μm).
REFERENCES


OBSERVATIONS OF NEW-PARTICLE FORMATION ALONG HORIZONTAL ROLL VORTICES

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Keywords: NEW-PARTICLE FORMATION, PLANETARY BOUNDARY LAYER, HORIZONTAL ROLL VORTICES, AIRBORNE MEASUREMENTS.

INTRODUCTION

New-particle formation (NPF) is a frequent phenomenon in the continental boundary layer and is an important source of climatically relevant aerosol particles (e.g. Kulmala et al., 2013). Significant local scale (1–10 km) spatial variation has been observed in the number concentration of freshly formed particles even inside a well-mixed boundary layer, especially in the horizontal direction (e.g. Väänänen et al., 2016).

In this study we analyzed airborne and surface-based measurements of aerosol particles. The aim was to identify regions where the nucleation mode particles had an increased number concentration and to explain why these regions occurred.

METHODS

A light Cessna 172 airplane and a Zeppelin NT airship were used in the airborne measurements. The airplane measurements were done in separate intensive campaigns between spring and autumn during the years 2013–2015 (Väänänen et al. 2016). The zeppelin measurements were done during the spring 2013 (Manninen et al. 2016).

Key aerosol instruments onboard the airplane were a TSI 3776 ultrafine condensation particle counter (>3 nm particle number concentration) and a homemade scanning mobility particle sizer (10–400 nm particle number-size distribution). The key aerosol instrument onboard the Zeppelin was a neutral cluster and air ion spectrometer (2–42 nm particle number-size distribution and 0.8–42 nm ion number-size distribution). These instruments allowed us to obtain the nucleation mode particle concentration (3–20 nm).

The airplane measurements consisted of flight legs flown perpendicular to the mean wind at different altitudes scanning the boundary layer and the lower free troposphere (~30 km horizontal and ~3.5 km vertical extension). The zeppelin measured helical vertical profiles over a smaller area inside the boundary layer (~5 km horizontal and ~1 km vertical extension). The airborne measurements were done in the vicinity of the SMEAR II field station in Hyytiälä southern Finland (61°51’N, 24°17’E), and were complemented by the station’s extensive aerosol measurements.

From the data we identified spatial regions where nucleation mode particles had an increased number concentration and analyzed these regions. Due to the properties of these regions, we hypothesized that they were caused by roll vortex enhanced NPF. Roll vortices are large systems of horizontal helical circulations in the planetary boundary layer (e.g. Etling and Brown, 1998). Rolls were identified from tower and airborne wind measurements, nearby weather radar measurements and satellite images. We compared the roll observations with the aerosol particle measurements in order to test the hypothesis.
CONCLUSIONS

We found that some (adjacent) roll vortices were able to enhance NPF along their length (Figure 1). The nucleation mode number concentration could increase 2–10 fold compared to the surroundings. Regions of nucleation mode particles that were characteristic of roll enhanced NPF occurred on 43% of NPF event days and 21% of “undefined” days measured (Figure 2). On one of the measurement days (May 8, 2013) the particle growth rate in the roll enhanced NPF was similar to the regional NPF event (~2 nm/h). Extrapolating the results to regional scale means that the roll enhanced NPF could significantly increase the aerosol particle number concentration over the boreal forest.

Our observations are supported by previous studies. Easter and Peters (1994) showed numerically that various flows in the atmosphere, including roll vortices, could enhance nucleation rate. Buzorius et al. (2001) observed that NPF events often coincided with the occurrence of rolls. The likely reason why rolls can enhance NPF was also identified in these studies. The rolls can efficiently transport condensable vapors and clusters to the top of the boundary layer where nucleation and cluster activation becomes more favorable due to cooler, more humid and possibly cleaner environment.

ACKNOWLEDGEMENTS

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Figure 1. The airplane’s flight track colored by (a) averaged vertical wind and (b) 3–20 nm particle concentration on August 21, 2015. The roll vortices

Figure 2. The dark red bars refer to all the measurement flights and the light red bars to days when regions of nucleation mode particles characteristic of roll enhanced NPF were observed.

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POLAR NIGHT GREENHOUSE GAS AND BLACK CARBON OBSERVATIONS AT THREE ARCTIC STATIONS: ICE BASE CAPE BARANOVA, TIKSI, AND PALLAS

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Keywords: GREENHOUSE GASES, AEROSOL PARTICLES, MEASUREMENTS, ARCTIC.

INTRODUCTION

Arctic environment is changing as a consequence of increasing concentrations of greenhouse gases in the atmosphere. The effect highlights as reduced ice cover extent in the Arctic Ocean. Black carbon emitted by combustion processes effectively warm atmosphere. In the Arctic, the effect is most pronounced in spring and beginning of summer, when it reduces the albedo of snow. Monitoring of greenhouse gases and climatically active aerosols is highly needed, the current observation network being insufficient for estimation of emissions and long-range transport of these climatically important factors and their effects including feedbacks from nature. This concern has been strongly expressed by the World Meteorological Organization (WMO) and the Arctic Monitoring and Assessment Programme (AMAP, 2015).

Finnish Meteorological Institute considers arctic monitoring very important and has invested greatly on observations at three Arctic sites: Pallas-Sodankylä, Ice Base Cape Baranova, and Tiksi. Pallas-Sodankylä, the flagship observatory of the Finnish Meteorological Institute is close to the year-round open Norwegian and Barents Seas. Ice Base Cape Baranova is at high latitude on Bolshevik island between the Kara and the Laptev Sea. Tiksi is located on the shore of the Laptev Sea close to the cold pole of the northern hemisphere. Very successful measurement programme in Russia is a result of fruitful scientific co-operation between the Finnish Meteorological Institute and the institutes of the Russian Hydrometeorological Service, Arctic and Antarctic Research Institute (AARI) in particular.

Atmospheric winter conditions are quite different at the three stations. Pallas-Sodankylä is very much affected by the open sea around Scandinavia. Winds, temperatures and stratification vary depending on the advection being either marine or continental. At Tiksi continental conditions prevail in winter but in summer open Arctic Ocean modify weather to be rainy and cloudy. At Ice Base Cape Baranova, stormy winds are frequent and temperatures may be higher compared to Tiksi when advection is from the Atlantic Ocean. In this presentation we compare meteorological conditions at the sites and show how concentrations of greenhouse gases and absorbing aerosols vary along with long-range transport from different kinds of source areas.

METHODS

We used observations from the three stations (Figure 1). In Pallas-Sodankylä, in-situ surface greenhouse gas and aerosol measurements are done at Pallas (67°58.40'N, 24°06.94'E) on an arctic hill. Total column measurements within TCCON network are conducted at Sodankylä. Research station "Ice Base Cape Baranova" is located on the high latitude of Bolshevik island between the Kara and the Laptev Sea. Tiksi is situated on the shore of the Laptev Sea close to the cold pole of the northern hemisphere. Very successful measurement programme in Russia is a result of fruitful scientific cooperation between the Finnish Meteorological Institute and the institutes of the Russian Hydrometeorological Service, Arctic and Antarctic Research Institute (AARI) in particular.
Baranova" (79°16.82′N, 101°37.05′E) is in the very northern part of the Bolshevik island to the north from Taimyr. Multiyear sea ice may exist there in late summer as well. Greenhouse gas and aerosol observations started in October 2015 in a specifically equipped container, which was shipped from Helsinki. Scientists from AARI conduct at this station biological, cryospheric, oceanic, and geophysical observations, in addition to the meteorological measurements. Tiksi (71°35.65′N, 128°53.27′E) is on the shore of the Laptev Sea not far from the Lena river delta (Uttal et al., 2013; Asmi et al., 2016). Verhojansk uplands and the eastern part of Siberian continent are located to the south from the station. The Laptev Sea is ice-covered from the end of October to July. Greenhouse gas and aerosol measurements began in July 2010.

Greenhouse gases were measured by Picarro G2401 or G2301 using WMO/CCL traceable calibration gases. Absorbing aerosol concentration (black carbon) was measured by MAAP, Thermo Sci. 5012, and aerosol scattering by Nephelometer, Ecotech 3000. In addition, at all sites we measured meteorological parameter including wind, air and soil temperatures, heat fluxes and radiation components.

For estimation of origin of air masses arriving at the stations, ten-day surface flux sensitivity maps were calculated by the atmospheric transport and diffusion calculation system SILAM, which uses ECMWF meteorological fields.

RESULTS

In Polar night conditions sun is not heating the surface but heat is lost by thermal radiation resulting in negative net radiation balance. In the atmospheric boundary layer stable stratification is formed inhibiting downward turbulent heat flux. Air temperature close to the surface decreases. Atmospheric synoptic scale disturbances, which have strong momentum flux, break stable stratification and heat is transferred to the surface increasing air temperature. As an example of meteorological conditions, one month period of air temperature and wind speed is depicted in Figure 2. Very low wind speeds and low temperature occur concurrently. Continental character of Tiksi is highlighted as long calm periods prevailing most of the time during the polar night. Synoptic disturbances are transported frequently from the Northern Atlantic and ice-free parts of the Arctic Ocean to the Ice Base Cape Baranova. Shorter distance to the ice-free sea
and higher vertical mixing by winds make Ice Base Cape Baranova warmer compared to Tiksi, in spite of the fact that Ice Base Cape Baranova is located 800 km closer to the North Pole.

![Graph showing wind speed and air temperature over December 2015 for Cape Baranova and Tiksi](image)

Figure 2. FMI atmospheric aerosol and GHG measurements in the Arctic. The new unit (in photo) was installed at Cape Baranova station.

Variations of greenhouse gas concentrations reflect emissions from the upwind source areas. Anthropogenic emissions vary seasonally less than natural emissions. Carbon dioxide is emitted from nature by respiration and microbial processes but not absorbed by photosynthesis outside growing season. Wetland methane emissions peak during warm summer but exist at lower intensity also in winter. Marine methane emissions are very low during the ice-covered period (Bertchet et al., 2016). In winter, methane and carbon dioxide concentrations are close to marine background level in air-masses from the North Atlantic. Atmospheric concentrations at Pallas and Ice Base Cape Baranova often reach this level (Figure 3). Air masses, which have elevated concentrations at Pallas, usually originate from the continental Europe. To Ice Base Cape Baranova the most important source area is western parts of Siberia, and to Tiksi the Republic of Sakha and long-range transported sources from western and southern parts of Siberia. Vertical diffusion and dilution of emissions is restricted by the very strong stable stratification over Siberia that is a reason for seemingly high background level at Tiksi.

Concentrations of greenhouse gases, carbon monoxide and black carbon vary depending on the origin of air mass. Ice Base Cape Baranova is located very well to observe background conditions in the Arctic Ocean (Figure 4). In December, concentrations of all species were higher when advection is from the continent. Carbon dioxide and methane have extensive natural emissions, because soils and plants respire and wetlands emit methane also in this time of year. In December, black carbon is from anthropogenic sources as well as carbon monoxide. Black carbon emissions from western Siberia seem to be high compared to those from eastern Siberia but less deposition during the shorter transport time may partly explain the difference.
Figure 3. Time series of concentrations of gases CO$_2$ and CH$_4$ in December 2015-January 2016 measured at the three study sites.

Figure 4. Time series of concentrations of gases CO$_2$ and CH$_4$ and CO and black carbon BC in December 2015 together with flux sensitivity source area maps calculated for moments indicated by the arrows.
CONCLUSIONS

The data from the three stations presented, offer new opportunity to estimate sinks and sources of greenhouse gases and radiatively active aerosols over the Arctic Ocean and high-latitude Eurasian continent as well as to estimate long-range transport of these species to the high Arctic. Atmospheric inversion modelling is being used in this task. Peculiar meteorological conditions in the Arctic, low height of the atmospheric boundary layer and strong stable conditions are difficult for meteorological and atmospheric diffusion and transport models. The meteorological and turbulence data collected at the sites will help to improve these models. This is the main aim of the soon starting year of polar prediction (YOPP), when meteorological observations will be intensified in the Arctic.

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REFERENCES


AIRBORNE OBSERVATIONS OF SMALL CLUSTERS

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Keywords: AIRBORNE, CLUSTERS, NUCLEATION, PSM.

INTRODUCTION

According to current understanding, atmospheric aerosol particle formation begins at the diameter of around 1.5 nm (Kulmala et al., 2013). Atmospheric particle formation occurs all over the world, under different environments as well as vertically from the ground level inside the planetary boundary layer to within the free troposphere. It is still unclear where, when and how the particle formation evolves spatially and temporally inside the planetary boundary layer and how well ground-based and airborne observations correspond to each other. Airmodus ltd has developed the Particle Size Magnifier (PSM) which is able to measure neutral aerosol particles starting at the diameter of 1 nm (Vanhanen et al., 2011). Here we present the first flight measurements in the lower atmosphere measuring with a PSM. Due to our instrument’s inlet line setup from the outside to the inside of the plane, the cut-off size of the PSM was around 1.5 nm during the flight measurements depending slightly on the ambient conditions which varied during the flight.

METHODS

An airborne platform was used to study new particle formation and growth of the particles in the lower atmosphere. Measurement flights were operated with a small Cessna 172 aircraft departing from Tampere-Pirkkala airport during two measurement campaigns in spring and August 2015. The flights were carried out above the SMEAR II station area (61°51’N, 24°17’E, 181 m above sea level), in Hyytiälä, Southern Finland with altitude range of 300–3000 m above the sea level, in order for the flight measurements to be comparable to ground level and tower (35 m) aerosol observations.

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 (including 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. The instrument setup contained also devices measuring meteorological parameters (pressure, relative humidity, temperature), and concentrations of H2O and CO2 gases. For instrumentation, see also Schobesberger et al., 2013 and Väänänen et al., 2016.

PRELIMINARY RESULTS

During both campaigns (25.5.–11.6.2015 and 13.8.–25.8.2015) the weather was favourable for the measurements - many sunny days, many NPF event days. As an example case, on 13.8.2015 a newly formed sub-3 nm particles were detected around noon at SMEAR II station (Fig.1). During the next hours, the particles were observed to grow to larger size classes (3–20 nm). At the same time, we performed two measurement flights (morning and noon) above the SMEAR II station. During these flights, the NPF event was detected in the lower troposphere, under 1000 m a.s.l. (Fig.2) inside the rising mixed layer. The higher concentrations of 1.5–3 nm size range clusters were detected especially in mixing layer, under the cloud base.
Figure 1. Total particle size distribution measured with DMPS in SMEAR II, Hyytiälä on 13.8.2015. Flight times are marked with vertical black lines in figure.

Figure 2. Total particle concentration (top) and flight altitude (bottom) during the two measurement flights on 13.8.2015. Particle concentrations were measured with PSM, uCPC and SMPS.

During the morning flight the cluster concentration (in size range of 1.5–3 nm) was high (~5000 cm\(^{-3}\)) whereas in the afternoon the newly formed clusters had grown in size and the concentration of 3–10 nm particles increased while cluster size concentration decreased. At the same time around 11 o’clock newly formed clusters started to grow toward larger sizes also in SMEAR II.
CONCLUSIONS

In this study, the Particle Size Magnifier was found to effectively measure also at different altitudes in the lower atmosphere. We observed newly formed clusters in airborne measurements successfully. According to this study, new particle formation event was detected spatially both on ground level and inside the planetary boundary layer at the same time.

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INTRODUCTION

To understand health risks and climate change caused by aerosols, good understanding of physical and chemical properties of aerosols is needed. One key aspect is to know the size of the particles. Need of knowing the particle size distribution arises from the diverse interactions of different sized particles. E.g. small particles can travel deeper into the alveolar area causing adverse health effects and bigger particles can act as Cloud Condensation Nuclei (CCN) and alter the radiative properties of clouds (Boucher, 2013). Differential mobility particle sizers (DMPS) offer a method to measure size distributions of aerosol populations. Operation of DMPS is based on electrical mobility of the aerosol particles. Aerosols of specific size are selected with Differential Mobility Analyzer (DMA) and the number concentration of selected size particles is thereafter calculated with Condensation Particle Counter (CPC). The voltage in DMA changes with time and as a result particle size distribution is obtained.

METHODS

The DMPS is built in an aluminium frame. It consists of DMA, high voltage source for DMA, blower for sheath air, High Efficiency Particulate Air (HEPA) filter, relative humidity (RH) sensor, sheath air dryer and sheath air flow meter. Other convertible instruments are CPC and radiation source. Figure 1 represents the schematics of the DMPS.

![Schematics of the differential mobility particle sizer](image)

Figure 1. Schematics of the differential mobility particle sizer. Numbers from 1 to 6 are differential mobility analyzer (DMA), blower, High Efficiency Particulate Air filter (HEPA), relative humidity (RH) sensor, sheath air dryer and sheath air flow meter respectively. R is radiation source, HV is high voltage source for DMA and CPC is condensation particle counter.
Upcoming test measurements include assuring tightness of the system and validation of the DMPS by comparing it with commercial instruments.

**SUMMARY**

Small particles below 10 nm behave and interact with other substances differently compared to particles over 1 micron which leads to the need of knowing the size distribution of aerosol populations. Differential mobility particle sizers provide a tool for investigation of particle size distributions. Upcoming step in the building process is to validate how this DMPS operates compared to commercial instruments.

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**REFERENCES**

TEMPERATURE BASED MECHANISTIC MODEL OF WINTER TIME DIAMETER CHANGES IN THREE TREE SPECIES REVEALS DIFFERENCES IN STEM ELASTICITY AND IN PLASMA MEMBRANE WATER PERMEABILITY

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Keywords: DIAMETER CHANGE, FREEZING, PERMEABILITY, ELASTICITY.

INTRODUCTION

Water relations in trees are profoundly affected by freezing in winter. When temperature decreases below zero water in extracellular spaces rapidly freezes, and living cells suddenly lose access to the previously abundant liquid water stored in apoplastic space. Living cells that have undergone freezing acclimation in autumn, avoid ice nucleation that leads to lethal intracellular freezing by supercooling and by having a high concentration of solutes in cell sap (Burke et al. 1976). Freezing of water in the apoplast also blocks water transport in the xylem conduits. Furthermore, living cells typically also experience a dramatic change in intracellular water relations as the water potential of the newly formed ice surrounding the living cells is very low. The water potential of ice decreases 1.22 MPa per 1 °C decrease in temperature (Rajashekar et al. 1982) and causes living cells to dehydrate, which is explained by the theory of extracellular freezing of living cells (Ameglio et al., 2001).

The dehydration of living cells is caused by net loss of water from the living cells through the plasma membrane towards lower water potential ice. Water always moves towards lower water potential through the semi-permeable membrane. The rate at which water moves through the membrane depends mainly on the permeability of the membrane and elasticity of the cells. Wintertime plasma membrane permeability and elasticity are important properties as they affect the frost hardness of the living tissue. Elasticity can be 13% - 304% higher for frozen than thawed woody parts (Umbanhowar et al. 2008).

Stem diameter change measurements have been extensively used to monitor growth and water relations in trees stems (e.g. Sevanto et al. 2011, Mencuccini et al. 2013). The method has been also used to study freezing in trees (e.g. Zweifel and Häsl er 2000, Lindfors et al. 2015). When tree is frozen stem diameter changes are thought to reflect mainly the changes in water content and turgor pressure of living cells in xylem, phloem and vascular cambium as changes in water tension in the xylem can be excluded as practically all apoplastic liquid water is frozen.

The aim of this study was to test quantitatively how well the theory of extracellular freezing explains diameter changes in trees in the winter when ice is present. This was accomplished with a mechanistic model that used temperature and the difference in equilibrium of water potential between cell sap and ice to explain the stem, xylem and phloem diameter change dynamics in trees. We also evaluated the parameters of the model to reveal differences in plasma membrane permeability and elasticity between three tree species when the tree is frozen. To our knowledge, these properties have not been attempted to be studied using stem and xylem diameter change measurements in winter conditions so far.

MATERIALS AND METHODS

Diameter changes of xylem and phloem were monitored for three different tree species. Diameter changes for Alnus glutinosa (var. pyramidalis) and Tilia x europaea (T. x vulgaris) were monitored in an urban experimental
site in Helsinki with 3 tree trees per species during early spring winter 2010. Two trees of Pinus sylvestris were monitored at SMEAR I Värriö site in North-Finland during the winter 2015-2016.

To quantitatively test the theory of extracellular freezing with diameter change measurements we derived a model that explained the diameter change dynamics with temperature driven changes in water content of living cells. Water content of the living cells changes as water potential of ice is linearly related to temperature (Rajashekar et al. 1982) and difference in water potential between cell sap in living cells and ice leads to net water movement through the plasma membrane towards lower water potential. The model (called the basic model from here after) was expressed as the following:

\[
\frac{dD_b}{dt} = \alpha(T - \beta D_b)
\]

Where \(D_b\) is the modeled diameter change and \(T\) is the temperature. Parameters \(\alpha\) and \(\beta\), which are fitted, are formulated as following:

\[
\alpha = \frac{LA}{V_b} (E_b - \pi^*) \\
\beta = \frac{D_bX}{(E_b - \pi^*)}
\]

where \(L\) is the plasma membrane permeability, \(A\) is the surface area of plasma membrane, \(V_b\) is the sum of volume of all living cells, \(E_b\) is the elastic modulus, \(\pi^*\) is the osmotic concentration before freezing and \(X\) is how much water potential of ice changes per change in temperature. Parameter \(L\) can also be solved from the formula as a function of parameters \(\alpha\) and \(\beta\). In the basic model parameters \(\alpha\) and \(\beta\) we assumed not to have temperature dependencies.

We also developed another version of the model called the ‘complex model’ to study temperature dependencies of parameters \(\alpha\), \(\beta\) and \(L\). The complex model had different parameters \(\alpha_1\) and \(\alpha_2\) (instead of parameter \(\alpha\)) depending whether simulated water potential of ice was lower or higher than water potential of living cells. In the hysteresis model parameters \(\alpha_1\), \(\alpha_2\) and \(\beta\) had linear temperature dependencies. We solved the models numerically using a simple (forward) finite difference scheme.

RESULTS

Both model were found be very successful in explaining diameter changes for xylem, bark and phloem. An example of comparison of measured and modelled stem diameter change are shown in figures 1. Modeled diameter changes followed measured diameter change data closely throughout the whole temperature range in the data sets. Good fit of the basic model with only two parameters provides already quantitative evidence for the first time how diameter changes can be explained with the theory of extracellular freezing.
The models enabled us to estimate permeability of plasma membrane and elasticity of xylem and phloem for the three tree species and the complex model reveal pattern of temperature dependencies of those parameters. Permeability of plasma membrane in xylem and phloem was highest for Pinus and lowest for Alnus. The complex model revealed temperature hysteresis in permeability of plasma membrane; permeability was higher for *Tilia* when water was moving inwards to living cells and lower when water was moving outwards from living cells. We also for the first time used diameter change measurements to estimate elastic modulus of a frozen stem.

**DISCUSSION**

We have shown how frozen stem diameter change can be modelled using the theoretical basis of extracellular freezing and temperature measurements. The models successfully matched measurements using a mechanistic approach in the case of all the three tree species. This provided quantitative evidence on the theory of extracellular freezing that is the prevailing theory explaining stem diameter dynamics in the winter and that water exchange through the plasma membrane is the primary process responsible for the observed changes in stem diameter in the case of frozen stem.

The permeability of plasma membrane was estimated for frozen xylem and phloem using diameter change measurements. Temperature hysteresis in the permeability of plasma membrane suggest that physical processes working in the cases when water potential of living cells is lower or higher of water potential of ice, may be
different. When water potential of living cells is lower than water potential of ice water leaves living cells in liquid phase and freezes outside the cells. However, when water potential of living cells in lower water moves into living cells but may move in the apoplast in liquid or gas phase, before entering the living cells. We have also shown that elastic modulus of xylem and phloem can be estimated using diameter change measurements. This approach has the advantage of being nondestructive. Amplitude of the elastic modulus was similar to estimates done with other techniques.

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LOW PLANT WATER STATUS DECREASES THE ICE NUCLEATION TEMPERATURE OF TREES

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Keywords: freeze-thaw cycle, freezing stress, ice propagation, winter embolism, winter tolerance

INTRODUCTION

Boreal trees experience frequent freeze–thaw cycles annually. Water in tree xylem and other apoplastic (i.e. outside the cells) spaces inevitably freezes when temperatures drop a few degrees below zero. Freezing of apoplastic sap causes two kinds of consequences for trees. First, gases dissolved in liquid water form bubbles during freezing, and these bubbles are at risk of expanding during thawing and blocking the water transport conduits by air (Sperry and Sullivan, 1992). This is called freeze-thaw embolism. The other important aspect of freezing stress experienced by trees is frost induced cellular damage. Cellular damage can be caused either by membrane rupture through symplastic (i.e. inside the living cells) ice crystal formation, or through extreme cell dehydration and plasmolysis caused by low water potential created by apoplastic ice (Ristic and Ashworth, 1993).

Previously we have found that apoplastic ice nucleation temperature of xylem is related to conduit size when branches are saturated with water (Lintunen et al. 2013). We found that the apoplastic freezing temperature of water in the xylem increases with increasing conduit size regardless of the species or tree part. We hypothesize that conduit size determines the size of the largest particles that are able to penetrate through the pit pores and catalyse ice nucleation; different sized organic and inorganic nuclei are commonly found in plants (Wisniewski et al., 2002). Thus apoplastic freezing temperature in xylem conduits determines the frozen time period and the number of freeze-thaw cycles a tree experience during winter.

In this work, we have studied the linkage of xylem water status with apoplastic ice nucleation temperature and the size and duration of the freezing exotherm, i.e. increase in xylem temperature in relation to ambient air temperature due to the energy released from freezing (Burke et al. 1976).

METHODS

We study 10 gymnosperms and 18 angiosperms species collected from an Arboretum in Helsinki in February 2016. The sampled branches were of fixed length of 8cm, their average diameter was 0.5cm and they were collected approximately at the same distance from the branch apex. Five branches of each tree species were collected on a same day, wrapped in plastic bags to avoid evaporation and brought to laboratory. As ice nucleation is a stochastic phenomenon and even an individual branch freezes in different temperatures during different freeze-thaw cycles (Lintunen et al. 2013), all branches were exposed to three freeze-thaw cycles with a fixed temperature decrease rate (Fig. 1) in a weather chamber. After the freezing experiment, the branches were saturated with water for 24 hours and the freeze-thaw cycles were repeated with the saturated branches. During the experiment, stem and ambient temperatures were measured with thermocouples to record the freezing exotherms. After the freezing experiments with fresh and saturated branches, the branches were dried in an oven for 48 hours at 65°C degrees to determine the relative water content of the fresh samples. Another set of branches was collected from the same species at te same location in the end of April 2016 to measure their relative water content during spring after the thawing of the soil, when their water content can be expected to be higher than in the winter time. A subsample of the species was frozen again in April and freezing exotherms were recorded. Conduit sizes of the branches will be measured during autumn 2016.

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The statistical analysis are based on mixed model with hierarchical data structure (observations within species and branches were treated as random factors).

**RESULTS AND DISCUSSION**

Ice nucleation temperature was significantly different for angiosperms and gymnosperms in winter and in spring. Gymnosperms froze at approximately 2 degrees Celsius lower temperatures than angiosperms in fresh status in both winter and spring, whereas gymnosperms froze at 0.5 degrees Celsius higher temperature than angiosperms in saturated status. This indicates that the difference in ice nucleation temperature between the angiosperms and gymnosperms is explained mainly by differences in water status when branches are of similar size. Accordingly, relative tissue water content was significantly higher for angiosperms than for gymnosperms both in winter and spring (Fig. 2A).

Increase in tissue water content explained increase in ice nucleation temperature from winter to spring and from fresh to saturated branch status (Fig. 2B). This suggests that decreased tissue water content in xylem during winter shortens the frozen period of trees (due to lower ice nucleation temperature) and allows especially the evergreens to photosynthesize on winter days when air temperature is slightly below zero Celsius (Lindfors et al. 2015).
Ice nucleation temperature is not correlated with the size of the freezing exotherm, but it is correlated to the duration of an exotherm (Fig. 3). Thus the lower the freezing temperature, the faster the freezing propagation. Also Kitaura (1967) and Hacker and Neuner (2007) have shown that the propagation rate of freezing in tree shoots is proportional to the degree of supercooling of the shoots. It is also known from freezing experiments with thin ice sheets that the faster is the ice propagation rate, the more and the smaller are the gas bubbles formed into the ice (Carte 1961); gas bubbles form into ice because gases that are soluble to liquid water are not soluble to ice. Thus our results together with these earlier results suggest that low ice nucleation temperature decreases the size of bubbles forming in the ice. This is essential for trees in cold regions as the risk of winter embolism formation in a given environment is determined by the bubble size, i.e. small bubbles decrease the risk of winter embolism formation (e.g. Pittermann and Sperry, 2006; Mayr and Améglio 2016).

Figure 3. Size (A) and duration (B) of freezing exotherms plotted against ice nucleation temperature during winter in fresh and saturated branches, and during spring in fresh branches.

Species-specific standard deviation of ice nucleation temperature was 46% higher between saturated branches (within a species) than within individual branches. The difference was not significant when branches were compared in fresh status due to high variation in branch water content.

To conclude, the apoplastic freezing temperature of water in the xylem decreases with decreasing conduit size and decreasing tissue water content, and thus species and tree parts with small conduits and less water go through less freeze-thaw cycles annually. The results show that apoplastic ice nucleation temperature is different for angiosperms and gymnosperms even when the conduit size is similar as angiosperms freeze approximately 2 degrees Celsius closer to zero Celsius when we compare branches of similar size collected near branch apex (the conduit sizes for different species are currently being measured). This difference is explained by the different tissue water status, but cannot be explained simply by the volumetric amount of water based on the classical nucleation theory.

ACKNOWLEDGEMENTS

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SATellite observed Aerosol effects on Warm Cloud Properties over Yangtze River Delta of China

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Keywords: Aerosol, Cloud properties, MODIS, CALIPSO, CloudSat.

INTRODUCTION

Aerosol impacts on clouds and precipitation has been reported to introduce the largest uncertainty in quantifying the anthropogenic contribution to climate change (IPCC, 2007). The processes, atmospheric aerosols change the cloud properties, are collectively referred to as aerosol indirect effect (AIE). Cloud droplet activation or more specifically the number concentration of cloud condensation nuclei is a direct link between aerosols and clouds and a key aerosol property affecting their interactions. The interaction mechanism between aerosols and clouds still remains one of the most uncertain processes in the global climate system and has been studied mainly through observations (Platnick et al., 2003; Koren et al., 2005, Krüger et al., 2011) and models (Suzuki et al., 2004; Quaas et al., 2009).

Resorting to a large amount of aerosol-cloud interaction data is best bet for us to better understand the aerosol indirect effect. By virtue of its large coverage areas, high spatial and temporal resolution, satellite-borne instruments have become a promising observational tool in revealing the interaction between aerosol and cloud. Based on multiple satellite observations, previous studies have shown that aerosol can affect cloud properties significantly. Satellite measurements suggest that cloud droplet effective radius (CDR) tends to be negatively associated with aerosol loading, which is consistent with the Twomey’s theory (Matheson et al., 2005; Meskhidze and Nenes, 2010; Koren et al., 2005). However, there are also positive correlations between CDR and aerosol optical depth (AOD) in some study areas, which were found both from observations and models, especially over land (Grandey and Stier, 2010; Yuan et al., 2008). In addition, the saturation changes in CDR with an increase of AOD are found in pervious literatures (Tang et al., 2014; Wang et al., 2015), which can be explained by the extended Twomey effect by Feingold et al. (2001). Likewise, the aerosol impacts on cloud optical depth (COT) is still poorly quantified. Costantino and Bron (2013) reported that the relationship between AOD and COT, which is positive or negative, depends on the balance between simultaneous CDR increase and cloud liquid water path (CWP) decrease when AOD increases. With regard to the impact of aerosol on cloud life cycle, it’s of great importance to explore the relationship between aerosol and cloud fraction (CF), because cloud fraction is highly associated with other cloud properties and it has a great effect on radiation (Gryspeerdt et al., 2016). Kaufman (2006) and Koren (2008) reported an increase in cloud cover with increasing aerosol loading and followed by an inverse trend due to absorption efficiency of aerosol. Therefore, the overall aerosol effect on the cloud properties and the magnitude of the aerosol influence are still unclear.
Satellite-observed aerosol and cloud have different vertical distributions and may not actually physically interacted. Costantino and Breon (2013) and Wang et al. (2015) found that aerosol indirect effect is more striking for mixed case clouds than separated case clouds when using MODIS data. These observed results evidence that the it is important to consider the relative altitudes of aerosol and cloud layers when estimating aerosol indirect effect.

The Yangtze River Delta is characterized by a variety of aerosol composition and increasing aerosol concentration in the last 2 decades, it is necessary to systematically investigate the aerosol-cloud interaction locally. Based on multi-sensor observed retrievals, this study aims to systematically examine the warm cloud parameters (CDR, CF, COT and CTP) response to aerosol enhancement. New insight lies in the focus on systematical understanding of AIE for mixed and seperated case clouds.

**METHODS**

The time of MODIS/Aqua overpassing the study area is around 13:30 local time, when continent warm clouds are more likely to be well developed. In order to better explore the interaction between aerosol and cloud, the MODIS/Aqua was selected as data source. In our study, MODIS AOD product (MOD04) is derived from cloud-free 500 m resolution data and aggregated to a resolution of 10 km×10 km. Here, we take the AOD as a proxy of aerosol burden for further aerosol indirect effects analysis. The cloud properties like CDR, CWP, COT, cloud top pressure (CTP) and cloud phase infrared (CPI) are obtained from Level 2 cloud product (MYD06), which are based on visible and near infrared wavelengths. The dataset of CloudLayerBase and CloudLayerTop from 2B-CLDCLASS-LIDAR, the latest version (R04) of CloudSat standard data products, is used in the present study. The data is in the CPR spatial grid with vertical and horizontal resolutions of approximately 480 m and 1.4×1.8 km, respectively. Three datasets of Layer_Top_Altitude, Layer_Top_Altitude and Layer_Top_Altitude, retrieved from CALIOP level 2 aerosol layers product (05kmALay), are used in the present study. Its footprint is very narrow, with a laser pulse diameter of 70 m on the ground. All MODIS/AQUA, CALIOP/CALIPSO, and CPR/CLOUDSAT are orbiting the Earth in the A-Train platform and cover the same scene of the Earth in one to two minutes. Therefore, time-coincidence of retrievals is assured when the datasets are extracted from the same date.

As it is difficult for MODIS to directly detect the aerosols located beneath a cloud layer, there is some cloud contamination when calculating AOD. To reduce the over-estimation of aerosols, cases with AOD greater than 1.5 is excluded. In this paper, we focused on warm clouds with CTP smaller than 700 hPa and CWP lower than 200 g m$^{-2}$ as most aerosols exist in the lower troposphere. In addition, only cases with CPI = 1 (liquid water cloud) were included. When CALIPSO detects the presence of aerosol, we average the MODIS aerosol retrievals within a radius of 50 km from the CALIPSO target. Like wise, we average the MODIS cloud retrievals within a radius of 5 km from the CALIPSO target.

According to the method by Costantino and Breon (2013), aerosol and cloud layers are considered physically interacting (well mixed) when the vertical distance between aerosol layer bottom (top) and cloud layers top (bottom) is smaller than 100m. On the contrary, the coincident samples with distance larger than 750m are assumed to be “well separated”. And the coincident samples with distance between 100 and 750m are defined as “uncertain” and excluded from further analysis.

**CONCLUSIONS**

Based on the near-simultaneous aerosol and cloud retrievals derived from MODIS, CALIOP and CloudSat products, we investigated the interaction between aerosol and cloud over Yangtze River Delta in summertime from 2007 to 2010. In terms of the relative altitude levels of aerosol and cloud layers, mixed case clouds and separated case clouds are defined. Statistical analysis has been used to examine the aerosol effects on cloud for seperated and mixed case clouds, respectively.
For the separated case clouds, we can see that cloud properties do not vary obviously with AOD no matter aerosol abundance is relatively low or high. The weak variation can be attributed to the fact that no aerosols subjected to the clouds microphysical process since there are no physically interactions between aerosol and cloud layers. For the mixed case clouds, cloud droplet effective radius initially decrease with increasing aerosol concentration and followed by an increase with higher aerosol concentration. Result is consistent with the Twomey’s hypothesise that more aerosol abundance lead to smaller cloud droplet effective radius given constant cloud water content. The positive AIE maybe caused by the microphysical processes, which is coupled with intense vapor competitions and smaller droplets evaporation as a result of high aerosols abundance. Also, CF shows an increasing trend when AOD increases under relative clean conditions (AOD < 0.4). Conversely, AOD and CF was negatively correlated under heavily polluted conditions (AOD > 0.4). This negative relationship can be put down to the dominate radiative process, which outweighs the microphysical process. Cloud optical depth is found to decrease with increasing aerosol concentration. We argue that the radiative effect and retrieval artifact due to absorbing aerosol may play a key role in the relationship. This effect can result in increased cloud evaporation and reduce cloud cover. Meanwhile, cloud top pressure tends to increase as aerosol concentration increase, indicating that the aerosol is prone to expand the horizontal extension.

Figure 1. Statistical relationship between cloud parameters and AOD retrievals in log-log scale over YRD for cases of separated and mixed aerosol-cloud layers, (a) correlation between CDR and AOD, (b) correlation between CF and AOD, (c) correlation between COT and AOD and (d) correlation between CTP and AOD. Error bars represent the confidence level of the mean cloud parameters’ value for each equally spaced AOD bin, from 0 to 1.5 (by step of 0.02). The lines indicate the corresponding aerosol cloud interaction strength.

ACKNOWLEDGEMENTS

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LONG-TERM IN-SITU MEASUREMENTS OF AEROSOL OPTICAL PROPERTIES IN HYyttiälä

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Keywords: AEROSOL, OPTICAL PROPERTIES.

INTRODUCTION

Aerosol particles affect the climate directly by scattering and absorbing radiation from the sun. Measurements of atmospheric aerosol optical properties are needed in defining the radiative forcing in an air column. Compared to greenhouse gases, aerosol particles have a large variability both in time and space and thus they’re still one of the largest uncertainties in calculating global radiative forcing (Boucher et al., 2013). Aerosol optical properties have been measured at the SMEAR II station for over ten years. In this study typical values in two size fractions, \( D_p < 1 \mu m \) (PM1) and \( D_p < 10 \mu m \) (PM10) are presented.

METHODS

The measurements presented in this study have been measured in SMEAR II station during 2006 - 2015. SMEAR II is located in Hyytiälä, Southern Finland (61°51’N, 24°17’E) and the station represents conditions in a boreal forest. Optical properties of particles smaller than 10 \( \mu m \) (PM10) have been measured from year 2006 and since 2010 also optical properties of particles smaller than 1 \( \mu m \) (PM1) have been measured. PM1 and PM10 have been measured by switching between PM1 and PM10 inlets for every 10 minutes.

The scattering and backscattering coefficients (\( \sigma_{\text{scat}} \) and \( \sigma_{\text{bscat}} \)) were measured at three wavelengths (450, 550 and 700 nm) with an integrating nephelometer (TSI model 3563). The truncation correction presented by Anderson and Ogren (1998) was applied for measured \( \sigma_{\text{scat}} \). The absorption coefficient (\( \sigma_{\text{abs}} \)) was measured with a seven wavelength (370, 470, 520, 590, 660, 880 and 950 nm) aethalometer (Magee Scientific model AE-31). Measured \( \sigma_{\text{abs}} \) was corrected for filter loading artefacts with an algorithm described by Arnott et al., (2005). Multiple scattering correction \( M \) in the algorithm was defined for 660 nm by comparing the \( \sigma_{\text{abs}} \) measured by aethalometer to \( \sigma_{\text{abs}} \) measured by Multi-Angle Absorption Photometer on 637 nm. Resulted \( M = 3.10 \) was then extrapolated to other wavelengths with a power function. The complex refractive index was calculated with an iteration algorithm that uses Mie-theory, the measured \( \sigma_{\text{scat}} \) and particle number size distributions in a similar manner as described by Virkkula et al. (2011). The size distributions were measured with a Differential Mobility Particle Sizer (DMPS) and an Aerodynamic Particle Sizer (APS). If the relative humidity of the sample air was higher than 40 \%, data was left out. All measurements were converted into STP conditions.

CONCLUSIONS

Time series of \( \sigma_{\text{scat}} \), \( \sigma_{\text{bscat}} \) and \( \sigma_{\text{abs}} \) for PM10 and PM1 are presented in figure 1. A linear fit was calculated for 1 hour averages of every variable and a slightly negative trend was found for all of them. Negative trends were a bit larger for PM1 which may due to shorter data sets.
Typical values and seasonal variation of PM10 optical properties in Hyytiälä have been presented before in Virkkula et al. (2011) and the results for PM10 were very similar in this study. The median values of different optical properties, which are derived from $\sigma_{\text{scat}}$, $\sigma_{\text{bscat}}$ and $\sigma_{\text{abs}}$, are shown for PM10 and PM1 in Table 1. The differences between the intensive optical properties of PM1 and PM10 can be explained by differences in size and composition. The seasonal variation for PM1 optical properties were similar to those of PM10.

The median values of different optical properties, which are derived from $\sigma_{\text{scat}}$, $\sigma_{\text{bscat}}$ and $\sigma_{\text{abs}}$, are shown for PM10 and PM1 in Table 1. The differences between the intensive optical properties of PM1 and PM10 can be explained by differences in size and composition. The seasonal variation for PM1 optical properties were similar to those of PM10.

![Figure 1. Yearly boxplots of $\sigma_{\text{scat}}$, $\sigma_{\text{bscat}}$ and $\sigma_{\text{abs}}$. Edges of a box represent 25th and 75th percentiles, the line in middle is the median, the circle is the mean and the whiskers represent 1st and 99th percentiles. The linear fit was determined for 1 hour averages of the dataset. P-value for every plot is < 0.01.](image)

<table>
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<th>PM10</th>
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<tr>
<td>Imaginary part of refractive index</td>
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<td>0.023</td>
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</table>

Table 1. Median values for different optical properties on green wavelength (550 nm) for both PM1 and PM1.
Seasonal variation of $\sigma_{\text{scat}}$, $\sigma_{\text{bscat}}$ and $\sigma_{\text{abs}}$ PM1/PM10 fraction is presented in figure 2. The fraction of PM1 $\sigma_{\text{scat}}$ and $\sigma_{\text{bscat}}$ is highest during summer and there’s minima during spring and autumn. For $\sigma_{\text{abs}}$ the median PM1/PM10 relation is 0.93 and there doesn’t appear any strong seasonal cycle. The small difference in absorption between PM1 and PM10 was expected since most of the absorbing particles are small ones. However the deviation is a lot larger during summer than in winter and there’s also values above 1. This may be due to low $\sigma_{\text{abs}}$ during summer and also due to higher $\sigma_{\text{scat}}$, since it’s taken into account in the Arnott correction algorithm.

![Figure 2. Seasonal variation of PM1/PM10 fraction of $\sigma_{\text{scat}}$, $\sigma_{\text{bscat}}$ and $\sigma_{\text{abs}}$. Edges of a box represent 25th and 75th percentiles and the line in middle is the median.](image)

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REFERENCES


SEASONAL COURSES OF METHANE FLUXES IN BOREAL TREES
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Keywords: CH₄ FLUX IN TREE STEMS, BIRCH, PINE, SPRUCE.

INTRODUCTION
Methane (CH₄) is the second most important greenhouse gas contributing to the acceleration of greenhouse effect and subsequent global warming. Boreal forests are considered to be a significant natural sink of CH₄ (Dalal and Allen, 2008) due to a predominant soil uptake of CH₄ from the atmosphere by CH₄ oxidizing (methanotrophic) bacteria (Smith et al., 2003). Therefore, the majority of studies have focused on quantifying the CH₄ exchange between boreal forest soils and the atmosphere. However, recent studies have shown that plants can significantly contribute to the CH₄ exchange between ecosystems and the atmosphere (Rusch and Rennenberg, 1998; Pangala et al., 2014, 2015; Machacova et al., 2013, 2016). Fluxes of CH₄ have been mostly studied on herbaceous plants, whereas investigations on trees, particularly boreal tree species, are still rare. Quantification and understanding these fluxes is, however, necessary for a correct global CH₄ inventory.

Therefore, seasonal CH₄ fluxes between stems of common boreal tree species – Scots pine (Pinus sylvestris), Norway spruce (Picea abies) and downy and silver birch (Betula pubescens, B. pendula) – and the atmosphere were determined. The specific objectives were to investigate (1) whether these tree species emit CH₄ to the atmosphere, (2) whether these fluxes have seasonal variation, and (3) whether soil water content affects the CH₄ exchange from trees.

METHODS
The measurements were performed on mature trees in the boreal forest surrounding the SMEAR II station in Hyytiälä (61° 51’ N, 24° 17’ E; 181 m asl) (Hari and Kulmala, 2005), southern Finland. Stem and forest floor fluxes of CH₄ were measured simultaneously over the whole year (from June 2014 to May 2015) using manual static chamber systems (for details of measurements see Machacova et al., 2014, 2016; Pihlatie et al., 2013). Changes in the CH₄ concentration, quantified by a gas chromatographic analysis (Machacova et al., 2016), were used to calculate the CH₄ fluxes.

Measurements were conducted at a naturally wet plot (annual mean soil volumetric water content (VWC) ± s.e., 0.81 ± 0.02 m³ m⁻³), at a moderately wet plot (0.40 ± 0.02 m³ m⁻³), and at a dry plot (0.21 ± 0.01 m³ m⁻³). The CH₄ exchange between the bottom part of the stems and the atmosphere was investigated in three pine, three spruce and three birch trees at the wet and moderately wet plots and in three pine trees at the dry plot, as birch and spruce were not present at this plot. Fluxes between the forest floor and the atmosphere were measured on three positions at the wet and moderately wet plots and on one position at the dry plot. The tree and stand characteristics are presented in Machacova et al. (2015). Parallel stem and forest floor measurements of all tree species and plots were conducted at least once per month, except on November 2014 and January 2015. The fluxes for these months were estimated using linear interpolation of fluxes from adjacent months. The fluxes, calculated by linear least square fits of the time series of CH₄ concentrations, are expressed as µg CH₄ per m² of stem or soil surface area, respectively, per hour.
RESULTS AND DISCUSSION

Our results show that mature boreal trees exchange CH$_4$ with the atmosphere throughout the whole year with minimum and maximum fluxes during dormant and vegetation period, respectively (Fig. 1a,b,c). The fluxes are further modulated by soil water content. Under high soil VWC, birch (i.e. mixture of $B$. pubescens and $B$. pendula) was found as the strongest CH$_4$ emitter among the tree species studied. However, the emission capacity of birch was closely connected to soil VWC with significantly lower fluxes at the moderately wet and dry plots. Accordingly to Evans (2003) we hypothesise a formation of aerenchyma system in birch roots under high VWC. Such aerenchyma system can substantially stimulate CH$_4$ transport from roots to the aboveground plant tissues, and subsequently lead to emissions to the atmosphere (Rusch and Rennenberg, 1998; Machacova et al., 2013). In contrast, we do not expect formation of an aerenchyma in the studied conifer trees (Evans, 2003), which is supported by lower CH$_4$ fluxes in pine and spruce (Fig. 1b,c) as compared with the broadleaved birch trees (Fig. 1a). Moreover, the differences in wood anatomy and further the gas diffusivity between broadleaved and coniferous tree species (Sorz and Hietz, 2006) might also explain the different flux capacities between the tree species. Similarly to stem fluxes, the forest floor fluxes were also modulated by soil VWC with predominant CH$_4$ emission under high VWC and uptake of CH$_4$ from the atmosphere into the soil under low VWC (Fig. 1d).

The tree species studied emitted CH$_4$ mainly during the vegetation season. Considerable emissions were, however, detected already from February onwards (Fig. 1a,b,c), probably due to a temperature increase and subsequent physiological activity of the trees and snow melting. This finding is supported by a minor rate of transpiration, important driver of CH$_4$ emissions, during wintertime. However, the forest floor fluxes were not affected by snow melting (Fig. 1d). From November to January, the stem CH$_4$ fluxes were low, but mostly positive under higher soil VWC. In August, the CH$_4$ fluxes from stems of birch and pine, and from the forest floor significantly decreased probably due to decline of soil VWC in this month (data not shown). Contrary to the other tree species studied, spruce CH$_4$ emissions were independent of soil VWC and delayed over the year (Fig. 1a,b,c). Further studies are needed to fully understand this phenomenon.
Figure 1. Annual course of CH$_4$ flux from stems of birch (a), spruce (b), and pine (c), and from forest floor (d) measured from June 2014 to May 2015. The fluxes are expressed as µg CH$_4$ m$^{-2}$ (of stem or forest floor area) h$^{-1}$. The solid line within the boxes marks median, the short dash line represents mean, the boxes boundary indicate 25th and 75th percentile, and the whiskers 10th and 90th percentile.
CONCLUSIONS

Both the broadleaved and the coniferous tree species studied emitted CH$_4$ from the stems into the atmosphere. Moreover, the trees emit CH$_4$ not only during the vegetation season, but also during wintertime. The stem fluxes were further modulated by soil VWC. Stem CH$_4$ emissions of trees thus may reduce the sink strength of soils in boreal forests. Therefore, it is necessary to incorporate stem CH$_4$ fluxes and their seasonal changes into the total estimates of CH$_4$ balance of boreal forests.

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GLOBAL VARIABILITY OF CLOUD CONDENSATION NUCLEI CONCENTRATIONS

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

INTRODUCTION

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

METHODS

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

Here we have used ECHAM5.5-HAM2 with model M7 microphysical aerosol model (Zhang et al., 2012). The model has been upgraded with a secondary organic aerosol (SOA) scheme including ELVOCs (Jokinen et al., 2015). Dust and sea salt emissions are calculated online, based on wind speed and hydrology. We calculate CCN at 0.2% supersaturation from the aerosol size distribution. The four experiments carried out are listed in Table 1. Each experiment is 11 years, analysed after a 6-month spin-up period. The MODIS CCN product (Terra platform) is used to evaluate model performance throughout 2000-2010. While optical remote observation of CCN column includes several deficiencies, the products serves as a proxy for changes during the simulation period. In our analysis we utilize the observed and simulated vertical column integrated CCN concentration (cm\(^{-3}\)), and limit our analysis only over marine regions.

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

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

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

![Figure 1. Correlation of simulated CCN (Control) and MODIS CCN calculated over annual averages during 2001-2010. Waved lines indicate areas where simulated intra-annual sea salt concentration correlates (R\(^2\)>0.1) with monthly MODIS CCN.](image)

We have focused our analysis on selected regions. Figure 2 shows annually averaged CCN and emission anomalies during 2000-2010 over Siberia (Sea of Okhotsk). The satellite observations indicate strong anomalies over the eastern outflow of Siberia: a steep decline from +22\% in 2003 to -35\% in 2004 followed by a steady rise until 2008. The MODIS CCN signal shows a clear drop in CCN concentration during 2008-2010, from +20\% to -22\%. The control model simulation captures extremely well the variability and the sign of the CCN anomaly (R = 0.85). The Siberian outflow is one of the few global regions where the "Control" simulation even overestimates the magnitude of the anomaly, especially during the negative phase of 2004-2007 when wildfire emissions in the region reach minimum values of the whole analysis period.

The model simulations with either fixed emissions or fixed meteorology reveal that the substantial drop in CCN during 2003-2004 is a combination of decreasing wildfire and BVOC emissions ("FixedMeteo", decrease in CCN from +10\% to -40\%) and meteorological patterns ("FixedEmis", decrease in CCN from +15\% to -20\%). The remarkably low anomalies of -30\% - -40\% due to emissions during 2004-2007 might explain the overestimation of the overall observed signal strengh.
Figure 2. Relative CCN and emission anomalies over outflow region of Eastern Siberia (120-180°E, 50-65°N). The emissions are divided into anthropogenic (fossil fuel, biofuel) and natural components. The shading over Control simulation and MODIS CCN indicates one standard deviation.

ACKNOWLEDGEMENTS

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THE FIRST NUCLEATION THEOREM, NEW PARTICLE FORMATION IN THE
ATMOSPHERE, AND THE MOLECULAR REALITY

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Keywords: NUCLEATION, NEW PARTICLE FORMATION, NUCLEATION THEOREM,
PHILOSOPHY OF SCIENCE.

INTRODUCTION

The first nucleation theorem, relating together the nucleation or new particle formation rate \( J \), gas-phase concentration(s) of the nucleating vapour(s)—in atmospheric sciences, one is typically interested on [\( \text{H}_2\text{SO}_4 \)], although concentrations of ammonia, amines, and iodic acid have also been under scrutiny—, and a number characteristic to the critical cluster that forms the bottleneck for the nucleation process, as the rate \( J \) is assumed to be dictated by the energetics of the critical cluster. Recently, there has been considerable criticism towards the application of the first nucleation theorem into atmospheric new particle formation (Kupiainen-Määttä et al., 2014), which largely stems from the fact that the observed new particle formation rate does not equal the hypothetical nucleation rate assumed in the derivation of the first nucleation theorem due to, for example, cluster loss (Malila et al., 2015), or failures of the field measurements to meet the other assumptions necessary for the first nucleation theorem to hold. Consequently, it has been noticed that one cannot resolve the mechanism of the atmospheric new particle formation based on the first nucleation theorem only. What has been left without further discussion are the philosophical implications of the application of the first nucleation theorem into new particle formation, either in the laboratory or in the field.

ASSUMPTIONS BEHIND THE FIRST NUCLEATION THEOREM

The first nucleation theorem can be seen as a manifestation of the general property of all extraordinary rate theories that one can use the theory “in reverse” to estimate the reaction parameters—effectively critical values of the various reaction coordinates—from measured rates (Peters, 2015). Indeed, already Nielsen (1964) gave two interpretations for the first nucleation theorem, first one in terms of the classical droplet model, where an application of the first nucleation theorem results in the (excess) number of molecules in the critical cluster, and another one in terms of chemical kinetics, where the number given by the first nucleation theorem is interpreted as the reaction order. Although conceptually the interchangeability of these two approaches is at the centre of the claimed unity of the reaction rate theory (Hettema, 2012), this division is actually underlines the whole field of nanocluster studies, even beyond rate theories, and can be generalised into macroscopic droplet or “top-down” and molecular “bottom-up” approaches (Bursten et al., 2016). (More recently, McGraw and Wu (2003) have introduced a third option, derivation based on physical kinetics that shares some features of both of these approaches.)

Irrespective of the details of the derivation leading to the first nucleation theorem, application of such a result into actual measured new particle formation rates implies an inherently positivistic philosophy. Somewhat surprisingly, no concerns on this have been presented in the literature, vice versa (e.g. Strey et al., 1994)! However, aforementioned fallacies of the first nucleation theorem (Kupiainen-Määttä et al., 2014) clearly indicate that such positivistic approach is not applicable to the atmospheric new particle formation studies, either. Besides such external factors, positivistic approach is also inappropriate form the viewpoint of unambiguous definition of the outcome of the first nucleation theorem due to multitude of its derivations with incommensurable assumptions (Fig. 1). Giving up some of these, e.g. the Szilárd–Farkas kinetics, allows us to search for parallel explanations for the observed characteristics of the atmospheric
new particle formation from the other sub-disciplines of science, while keeping the caveats of positivistic thinking at our mind.

Figure 1. An Euler diagram depicting the critical assumptions for various derivations of the first nucleation theorem presented in the literature: yellow shading implies a complete thermalisation of the forming cluster via heat bath provided by an inert carrier gas, green an ideal vapour phase, blue an immobile cluster, red an incompressible cluster, and grey discrete dynamics (in contrast to the assumption of a continuous cluster-size variable). Derivations given in italics can be seen as direct consequences of the law of mass action.

INSIGHTS FROM CONDENSED MATTER STUDIES: NON-CLASSICAL NUCLEATION

In condensed matter physics, there has recently been considerable interest on nucleation processes that do not follow the classical nucleation picture based on the Szilárd–Farkas or monomer kinetics and the concept of an unambiguous, single transition state for the process. Such processes have been categorised under the term non-classical nucleation (e.g. Gebauer and Cölfen, 2011) and may consist of various steps, including e.g. sub-critical cluster coagulation that again renders the first nucleation theorem obsolete (Vehkamäki et al., 2012). (Laaksonen and Malila (2016) have recently successfully adopted such a description for the heterogeneous nucleation of water vapour on atmospheric nanoparticles.) Laxson and Finke (2014) have argued that for non-classical nucleation processes, one should discard the classical concepts of reaction order and the critical size, and replace those with the concepts of kinetically effective and the first observable nuclei; in case of atmospheric new particle formation, exponent from the slope analysis should according to them be interpreted as the kinetically effective nucleus. These concepts, however, are also applicable to quite idealised nucleation processes only, as they are not, for example, directly applicable to cases with sub-critical cluster losses.

Based on field measurements, it has been argued that atmospheric new particle formation is a non-classical nucleation process (Kulmala et al., 2013). As these measurements, for neutral clusters, rely heavily on instruments such as mass spectrometers (Junninen et al., 2010), where clusters are first ionised and then exposed to vacuum, thereby potentially inadvertently altering the cluster composition, and particle size magnifiers (Vanhanen et al., 2011) that potentially can stabilise clusters otherwise not directly relevant for the nucleation process, these conclusions may not be seen utterly conclusive. Consequently, there are continuous efforts to model these processes in order to obtain a more complete molecular-level picture of the atmospheric new particle formation phenomena. Such modelling studies, however, are as
well prone to the positivistic fallacy, which should be taken into account when considering the theoretical framework to interpret the modelled results.

A REMARK FOR LARGE-SCALE MODELLING STUDIES

Based on a naïve interpretation of the field measurements, atmospheric new particle formation rates have been often parametrised into models using activation and kinetic descriptions (Kulmala et al., 2006). Although such simplified models have their own pragmatic merit (see Hoffmann et al., 1997, for a discussion of a related case of atmospheric chemical reactions), most notably allowing models with reasonable computational costs, they also exemplify the impossibility to verify or validate a numerical model in atmospheric sciences (Oreskes et al., 1994). Consequently, results of such parametrisations in cases where they cannot be immediately compared with the actual measurements need to be regarded cautiously, especially when communicating to non-specialists, as they may not reflect the actual nucleation processes taking place at the molecular level.

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REFERENCES


EFFECTS OF WEATHER FRONTS ON TURBULENT FLUXES OF ENERGY AND CARBON DIOXIDE MEASURED OVER A LAKE

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Keywords: EDDY COVARIANCE, LAKE-ATMOSPHERE EXCHANGE, HEAT FLUXES, CO2 FLUX

INTRODUCTION

Advancing our understanding on physical processes controlling turbulent exchange of energy, carbon dioxide, and other trace gases over lacustrine systems is crucial in order to improve climate and weather forecast models. Lakes have different albedo, lower surface roughness and greater effective heat capacity than surrounding land areas. These properties affect regional climate and energy budgets (Dutra et al., 2010). Moreover lakes are able to process large amounts of organic carbon and their importance in terrestrial carbon cycle and climate change issues is well recognised (Battin et al., 2009). Besides biogeochemical supply of dissolved carbon, CO2 emission from inland waters depends on atmospheric forcing, which enhance water turbulence and upwelling of dissolved carbon rich water from deeper depths. Recently using direct eddy covariance measurement in Lake Kuivajärvi (Finland), we have demonstrated that the gas transfer velocity does not depend only on wind speed (Cole and Caraco 1998), but also the buoyancy-induced turbulence during cooling periods is an important driver (Heiskanen, 2014; Mammarella et al., 2015). Here, we try to look in more details into this dynamics, showing one example of how weather fronts play an important role in controlling sensible heat (H), latent heat (LE) and CO2 fluxes.

METHODS

Energy and CO2 exchange has been monitored in Lake Kuivajärvi, located close to the Hyytiälä Forest Field Station, since 2010. Lake Kuivajärvi is a small humic boreal lake extending about 2.6 km in North/West-South/East direction and it is a few hundred meters wide (Fig. 1). The measurement platform is located approximately 1.8 km and 0.8 km from the Northern and Southern shorelines, respectively. The lake has a maximum depth of 13.2 m, and the depth at the location of the platform is 12.5 m.

The eddy covariance system on the platform includes an ultrasonic anemometer (Metek USA-1, GmbH, Germany) to measure the three wind velocity components and sonic temperature, and the enclosed-path infrared gas analyser Licor 7200 (LiCor Inc., Lincoln, NE, US) that measures CO2 and H2O concentrations. Starting from June 2012, the CH4 turbulent fluctuations are also measured by using the fast response gas analyser G1301-f (Picarro Inc., USA). All data were sampled at 10 Hz and the gas inlets were located at 1.5 m above the water surface close to the sonic anemometer.

The eddy covariance fluxes were calculated as 30 min block averaged co-variances between the scalars (or horizontal wind speed) and vertical wind velocity according to commonly accepted procedures (Mammarella et al., 2015; Mammarella et al., 2016).

Auxiliary data are continuously measured in proximity of the platform (5 sec sampling frequency), and they are water CO2 and temperature profiles, radiation components, air temperature and relative humidity (see Mammarella et al, 2015 for more details).
Fig 1. Location and bathymetric map of Lake Kuivajärvi. The wind is blowing most of the time along the lake, as shown by the dark arrows in the map. The lower photo shows the raft with measurement systems.

CONCLUSIONS

Figures 2 and 3 show the time series of some meteorological parameters and fluxes measured at Lake Kuivajärvi during the period 30\textsuperscript{th} of May – 15\textsuperscript{th} of June 2016. The first three days are characterized by southerly light wind up to 3 m s\textsuperscript{-1}, clear sky and warm air temperatures reaching more than 20\textdegree C during the day (Fig.2 upper and middle panels). At this time of the year, the lake is already thermally stratified, as clearly seen from the water CO\textsubscript{2} profile (Fig.2 lower panel). Turbulent fluxes of H and LE have a diurnal cycle, with a phase and amplitude clearly different from those typically found over land. Small magnitudes of H and LE during the first three days (Fig.3) reflect small differences between air and water temperatures, as well as moderate values of wind speed (Mammarella et al., 2015).

On 3\textsuperscript{rd} of June, the wind changes from southerly to northerly direction, the wind speed increased and the air temperature dropped down (Fig.2). Such synoptic weather events associated with cold front passage caused a pulse in H and LE fluxes, whose magnitudes reach positive values well above typical conditions for this period (Mammarella et al., 2015). The lake started to loose heat, and the surface water temperature decreased from 22\textdegree C to 14\textdegree C in less than one week. This cooling event caused the mixing of the water column and following upwelling of CO\textsubscript{2} from deeper layer to the water surface (Fig. 2). As a result, enhanced emission of CO\textsubscript{2} is clearly seen during this period, especially on 6\textsuperscript{th}, 9\textsuperscript{th}, 11\textsuperscript{th} and 12\textsuperscript{th} of June 2016. This simple case study, based on continuous observations, shows the tight connection between atmospheric forcing, thermal dynamics of water column and gas exchange at the air-water interface.
Fig. 2. Two week time series of wind speed and direction (upper panel), air and water temperature (middle panel) and water CO$_2$ concentrations at different depths (lower panel) measured in 2016 at Lake Kuivajärvi.

Fig. 3. Two week time series of sensible heat flux ($H$, red line), latent heat flux ($LE$, green line) and carbon dioxide flux (black line) measured in 2016 at Lake Kuivajärvi.

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IDENTIFICATION OF DIFFERENT STATES OF MIXING WITHIN A CONTINENTAL BOUNDARY LAYER IN A BOREAL FOREST ENVIRONMENT

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\textsuperscript{3}Finnish Meteorological Institute, Finland.
\textsuperscript{4}University of Reading, UK.

Keywords: BOUNDARY LAYER, TURBULENCE, DOPPLER WIND LIDAR.

INTRODUCTION

To better understand the chaotic and highly varying mixing processes within the boundary layer (BL) in different regions, the state of mixing can be divided into finite number of classes. Harvey \textit{et al.} (2013) proposed a BL classification method, which covered a number of mixing states where clouds where present within the BL, but only two cases where clouds were not present.

With improved methods for obtaining lidar quantities with significantly lower uncertainties, the identification of the sources causing mixing can be expanded significantly. Also, additional sources can be differentiated leading to a wider understanding which parts of the atmospheric profile are connected to the surface.

In addition, different weather forecast and climate models require different input parameters on the low level winds and turbulence. Another goal of our work is to provide parameters, which are obtained with Doppler wind lidar, that can be used as inputs by the different models.

METHODS

The Halo Photonics Doppler lidar is a commercially available instrument and has been developed to perform continuous and autonomous long-term measurements (e.g. Pearson \textit{et al.}, 2009). The instrument emits laser pulses in the near infrared spectral region at 1.5 \mu m, and outputs a profile of back-scattered light intensity, in terms of signal-to-noise ratio (SNR), together with a radial Doppler velocity determined from the Doppler shift of the back-scattered light. Horizontal wind speeds can be determined from combining orthogonal beams when scanning off-vertical. If the telescope function is known, the attenuated backscatter coefficients can be calculated (Hirsikko \textit{et al.}, 2014).

It is important to acknowledge that any error in the SNR will transfer to the Doppler velocity measurement uncertainty (Manninen \textit{et al.}, 2016). Thus, correcting for the artifacts present in the background SNR is essential.

From the Halo Doppler lidar measurement, several quantities (and their uncertainties) can be then calculated, such as the top of the aerosol layer (note: not the height of the BL), vertical velocity skewness, turbulent kinetic energy dissipation rate (O’Connor \textit{et al.}, 2010), and the vector wind shear.
CONCLUSIONS

The preliminary results can be seen as a proof-of-concept (Fig. 1). The method works well and can be applied routinely but there is still plenty of potential additions and fine tuning to perform. Despite much higher data availability within the BL after applying the background correction, the low aerosol load in boreal forest environments still causes uncertainties for the identification. Future work will concentrate on further developing the method and reducing the uncertainties.

Figure 1. Lidar quantities and the source for turbulence identification mask (bottom left) on 11 September 2015 at Hyytiälä, Finland.

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REFERENCES


Keywords: PAHS, OFFICES, OCCUPATIONAL EXPOSURE, FLOOR DUST.

INTRODUCTION

People spend about one third of their time at work/school, where a vast range of equipment is used such as printers, photocopiers, computers and etc. These equipments are thought to be a considerable source of air pollutants that settle down into floor dust (Ren et al., 2006; He et al., 2007; Koivisto et al., 2010; Hussein, 2014). Regarding the content of office floor dust, the most frequent and hazardous compounds are polycyclic aromatic hydrocarbons (PAHs). PAHs are products of the incomplete combustion of organic matters and they could be either natural or anthropogenic (Kameda et al., 2005). According to our knowledge, PAHs analysis in floor dust have been given little attention in Middle East. Therefore, in this study we determined the floor dust PAHs concentrations inside lecture rooms, offices and workshop areas at the University of Jordan, Amman, Jordan. We focused on the identification of the following 13 priority PAHs: Phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[j]fluoranthene (BjF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP). Moreover, we evaluated the occupational health exposure to PAHs inside that educational environment.

METHODS

The floor dust samples were collected on the 6th of April 2015. The building itself is naturally ventilated. Floor dust sample collection procedure for office floor dust was similar to the one for household dust in Amman (Maragkidou et al., 2016). The dust samples were gathered using one regular vacuum cleaner. We placed the vacuum dust bags made of nylon (25um-155mmX73/38mm, Allied Filter Fabrics Pty. Ltd) inside the tube of the vacuum cleaner, after the main façade. It should be noted that in case of a bare floor, the vacuuming of the sampled surface area lasted for about 2 minutes, otherwise (smooth floor), this procedure lasted for about 4 minutes. Overall, 10 floor dust samples were collected during rush hour (i.e. between 10 am to 2 pm) from offices, lectures rooms and two workshop areas from the Department of Physics of the University of Jordan. After the collection, the dust bags were sealed in a nylon bag that was closed thoroughly. During dust sampling periods, the cleaning staff of the building was instructed to execute their routine daily cleaning activities normally as they did in general.
The location, the surface area, the number of the floor and the surface type of the places where the dust samples were collected at the Department of Physics of the University of Jordan are given in Table 1. Offices 303 (P303) and 209 (P209) had blackboards hanging on the wall, therefore the floor dust samples collected from these offices were affected, in addition to the content of the floor dust, by different components consisting chalk which used to fall from the blackboard to the floor.

<table>
<thead>
<tr>
<th>Code</th>
<th>Location of dust sampling</th>
<th>Surface area (m²)</th>
<th>Floor</th>
<th>Surface type</th>
</tr>
</thead>
<tbody>
<tr>
<td>L230</td>
<td>Lecture room 230, Physics Department</td>
<td>2.70 × 1.35</td>
<td>1st floor</td>
<td>Bare floor</td>
</tr>
<tr>
<td>C1</td>
<td>Corridor, Physics Department</td>
<td>1.80 × 3.00</td>
<td>1st floor</td>
<td>Bare floor</td>
</tr>
<tr>
<td>BC</td>
<td>Big Corridor, Physics Department</td>
<td>2.70 × 2.70</td>
<td>Ground floor</td>
<td>Bare floor</td>
</tr>
<tr>
<td>L102</td>
<td>Lecture room 102, Physics Department</td>
<td>3.90 × 1.50</td>
<td>Ground floor</td>
<td>Bare floor</td>
</tr>
<tr>
<td>P300</td>
<td>Office 300, Physics head of the Department</td>
<td>3.00 × 1.00</td>
<td>2nd floor</td>
<td>Carpet</td>
</tr>
<tr>
<td>P303</td>
<td>Office 303, Physics Department</td>
<td>1.50 × 1.50</td>
<td>2nd floor</td>
<td>Carpet</td>
</tr>
<tr>
<td>P200</td>
<td>Office 200, Physics Department</td>
<td>1.50 × 1.50</td>
<td>1st floor</td>
<td>Carpet</td>
</tr>
<tr>
<td>P209</td>
<td>Office 209, Physics Department</td>
<td>3.00 × 3.00</td>
<td>1st floor</td>
<td>Bare floor</td>
</tr>
<tr>
<td>WSa</td>
<td>Workshop, big area, Physics Department</td>
<td>1.50 × 1.50</td>
<td>Ground floor</td>
<td>Bare floor</td>
</tr>
<tr>
<td>WSb</td>
<td>Workshop, welding area, Physics Department</td>
<td>1.50 × 1.50</td>
<td>Ground floor</td>
<td>Bare floor</td>
</tr>
</tbody>
</table>

Table 1. Location, surface area, number of the floor and surface type of the places where the dust samples were collected spaces in the Department of Physics of the University of Jordan.

RESULTS AND CONCLUSIONS

GC-MS analysis indicated that PAHs concentrations ranged from 14 ng/g to 969 ng/g (Figure 1 and Table 2). Office 300 (P300) recorded the highest total PAHs concentration (5246 ng/g), followed by office 200 (P200) (total PAHs concentration = 5152.65 ng/g) and 1st floor corridor (C1) (total PAHs concentration = 4364 ng/g) at the Department of Physics (Table 2). This could be justified by the fact that inside these areas (P200, P300, C1) smoking activities took place. However, WSB, WSA and L102 presented, in ascending order, the lowest total PAHs concentration during the measurement day (Table 2).

Moreover, P200 recorded the highest PAHs concentrations for seven PAHs (Figure 1); anthracene, benz[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[j]fluoranthene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene (Table 2). P300 and C1 followed exhibiting the highest PAHs concentrations for three PAHs, separately (Table 2). Amongst all PAHs concentrations, fluoranthene, chrysene, pyrene and phenanthrene monitored the highest values (around 969, 763, 723 and 710 ng/g, respectively) (Figure 1 and Table 2), mainly due to students’ frequent entry and activities, smoking occurring inside and outside those areas, as well as the constant operation of office equipment (copy machine, computers, etc.).

Keeping in mind that university staff was exposed to PAHs via ingestion, we calculated the BaP toxic equivalent (BaPE) factor to PAHs, the estimated daily intake (EDI) and the estimated daily intake based on BaP toxic equivalent values (EDI as BaPE).
According to Table 3, total BaPE values for dust samples collected from lecture rooms, offices and workshop areas at the Department of Physics ranged from 25.52 ng/g to 384.68 ng/g. The lowest and the highest BaPE values were detected in WSa and C1, respectively. Concerning other studies focused on health risk assessment, Peng et al. (2012) indicated that total BaPE values for 13 out of 18 PAHs measured in lecture theatres and dining halls in Shanghai’s universities were around 655.220 and 705.60 ng/g, respectively (Table 3). In addition, total BaPE values measured in six different workplaces (including commercial office, secondary school, shopping mall, hospital, electronic factory and manufacturing plant) in Hong Kong (Kang et al. 2010; Peng et al. 2012) were much higher than the ones in our study (around 541.80 ng/g). With respect to health risks due to exposure to household dust, total BaPE values in Berlin and in the Netherlands (Fromme et al., 2004; Oomen et al., 2008) were roughly larger than the ones in our research; around 467.20 ng/g for Berlin and 448.00 ng/g for the Netherlands (Table 3).

EDI values ranged from 0.01 to 0.69 ng/kg-bw/day, whereas total EDI values were as high as 3.75 ng/kg-bw/day and as low as 0.51 ng/kg-bw/day. Previous studies (Kang et al. 2010; Peng et al., 2012) evidenced that total EDI values in lecture theaters and dining halls in Shanghai’s universities as well as in six different workplaces in Hong Kong were exceptionally higher than the corresponding ones in our research (Table 3). The same applied to EDI values estimated based on BaPE values.

Specifically, total EDI as BaPE values in our case ranged from 0.02 to 0.27 ng/kg-bw/day. Nonetheless, total EDI as BaPE in lecture theaters and dining halls in were equal to 0.52 and 0.56 ng BaP/kg-bw/day, respectively, whereas total EDI as BaPE value in Hong Kong was 0.43 ng BaP/kg-bw/day. Furthermore, EDI values estimated based on BaPE values in studies made in Berlin (Fromme et al., 2004) and in the Netherlands (Oomen et al., 2008) were slightly greater than the ones in our work; 0.32 ng BaP/kg-bw/day both in Berlin and in the Netherlands (Table 3).

However, taking into consideration that the maximum allowable daily intake in air ranged from 1.00 ng BaP/kg-bw.day (females) to 1.29 ng BaP/kg-bw.day (males) (according to the standard limits of 6 ng/m³ as BaP for PAH in the air set by the European Union), it is obvious that human health from exposure to PAHs via dust ingestion inside the Department of Physics at the University of Jordan was at an insignificant risk.

![Figure 1. PAH concentration content [ng/g] at the Department of Physics, University of Jordan, Amman.](image-url)
### Table 2. PAHs concentrations [ng/g] in the floor dust collected at the Department of Physics, University of Jordan, Amman, where below detection limit concentrations were marked as --.

<table>
<thead>
<tr>
<th></th>
<th>P200</th>
<th>P209</th>
<th>P300</th>
<th>P303</th>
<th>L102</th>
<th>L230</th>
<th>WSa</th>
<th>WSB</th>
<th>BC</th>
<th>CI</th>
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<tbody>
<tr>
<td>PHE</td>
<td>380</td>
<td>438</td>
<td>410</td>
<td>220</td>
<td>186</td>
<td>316</td>
<td>171</td>
<td>190</td>
<td>471</td>
<td>710</td>
</tr>
<tr>
<td>ANT</td>
<td>168</td>
<td>105</td>
<td>106</td>
<td>84</td>
<td>77</td>
<td>99</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>74</td>
</tr>
<tr>
<td>FLA</td>
<td>810</td>
<td>393</td>
<td>969</td>
<td>490</td>
<td>186</td>
<td>264</td>
<td>251</td>
<td>106</td>
<td>519</td>
<td>632</td>
</tr>
<tr>
<td>PYR</td>
<td>672</td>
<td>275</td>
<td>723</td>
<td>439</td>
<td>182</td>
<td>243</td>
<td>147</td>
<td>205</td>
<td>489</td>
<td>517</td>
</tr>
<tr>
<td>BaA</td>
<td>487</td>
<td>153</td>
<td>467</td>
<td>283</td>
<td>107</td>
<td>141</td>
<td>--</td>
<td>--</td>
<td>224</td>
<td>374</td>
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<tr>
<td>CHR</td>
<td>763</td>
<td>199</td>
<td>739</td>
<td>534</td>
<td>168</td>
<td>199</td>
<td>147</td>
<td>43</td>
<td>334</td>
<td>496</td>
</tr>
<tr>
<td>BbF</td>
<td>603</td>
<td>167</td>
<td>693</td>
<td>500</td>
<td>159</td>
<td>264</td>
<td>251</td>
<td>106</td>
<td>519</td>
<td>632</td>
</tr>
<tr>
<td>BjF</td>
<td>258</td>
<td>78</td>
<td>241</td>
<td>183</td>
<td>73</td>
<td>86</td>
<td>32</td>
<td>14</td>
<td>110</td>
<td>184</td>
</tr>
<tr>
<td>BaP</td>
<td>222</td>
<td>98</td>
<td>253</td>
<td>182</td>
<td>69</td>
<td>101</td>
<td>--</td>
<td>22</td>
<td>137</td>
<td>255</td>
</tr>
<tr>
<td>IcdP</td>
<td>307</td>
<td>94</td>
<td>252</td>
<td>210</td>
<td>83</td>
<td>129</td>
<td>93</td>
<td>63</td>
<td>123</td>
<td>213</td>
</tr>
<tr>
<td>DahA</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>33</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>89</td>
</tr>
<tr>
<td>BghiP</td>
<td>307</td>
<td>94</td>
<td>252</td>
<td>210</td>
<td>83</td>
<td>129</td>
<td>93</td>
<td>63</td>
<td>123</td>
<td>213</td>
</tr>
<tr>
<td>Total PAH</td>
<td>5153</td>
<td>2125</td>
<td>5246</td>
<td>3444</td>
<td>1445</td>
<td>1940</td>
<td>1246</td>
<td>714</td>
<td>2916</td>
<td>4364</td>
</tr>
</tbody>
</table>

Table 3: Estimated daily intake (EDI) [ng/kg-bw/day], total estimated daily intake (total EDI) [ng/kg-bw/day], EDI estimated based on BaPE (EDI as BaPE) [ng/kg-bw/day] and total BaPE values [ng/g] of PAHs via dust ingestion in the Department of Physics at the University of Jordan, in Shanghai’s universities, in Hong Kong, in Berlin and in the Netherlands.
ACKNOWLEDGEMENTS

This work was supported by the European Commission FP7 (FP7-PEOPLE-2012-ITN) Marie Curie ITN project (no. 315760, HEXACOMM), the Faculty of Scientific Research of the University of Jordan and the Academy of Finland Centre of Excellence (grant no. 272041).

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INTRODUCTION

Ground vegetation cover and its composition in a forest are a result of many above- and belowground constituents. Tree species composition, their size distribution, and the combination of these two affect the light environment and micrometeorology of a forest. Soil properties, both the structural and nutritional one, have an important role as well. Nitrogen (N) is usually limiting growth in boreal forests, and has thus been studied much (e.g. Helmsaari 1995, Nilsen 2001, Korhonen et al. 2013, Coucheney at al. 2013). Boreal forests can, however be also limited by phosphorus (P) (Shaver et al. 1998, Moilanen et al. 2010, Vadeboncoeur 2010, Crowley et al. 2012). Phosphorus is one of the major nutrients that plants require for their growth and it is specifically important during the early growth and development (Raghothama 1999). It is the most immobile major nutrient and only directly available to plants as inorganic phosphates (Pi) H2PO−4 and HPO2−4 (Hinsinger 2001). Soil total P content may thus be high even if P is not present in the correct form for plants.

In changing climate the nutrient cycling of forests will most likely be altered. According to some studies (Rustad et al. 2001, Robinson et al. 2002) warming may accelerate microbial activity and decomposition in the soil, which can release more nutrients than before. On the other hand soil warming can reduce the amount of soil water, which may slow down decomposition rates and deplete nutrient release (Hicks Pries et al. 2013).

Our study area is located in Eastern Lapland, near Sokli, where a large carbonatite massif lies. The massif is rich in P and has been planned for several year to be utilized as material for fertilizers by different mining companies. Currently the mining plans have been put on hold. In addition to the massif there are so-called hot spots of P in various places. Part of our sites have been set up to places which, by visual estimation of vegetation, were evaluated as possibly high in soil P. These sites had Betula pubescens as the dominating tree species and a greater number of species in the ground vegetation than the other sites. The rest of the sites are in forests with a forest vegetation cover typical for the region. This arrangement allowed us to compare different levels of soil P without organizing any fertilizer experiments. Our aims were first to examine whether we truly had found sites 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 analyzed total elemental concentrations of soil, needle and leaf samples and mapped ground vegetation covers and tree compositions at 16 different research sites in and around Värrö Strict Nature Reserve, Eastern Lapland. Also rainwater and snow samples were taken monthly during October 2014-September
2015 in order to determine 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 mainly in 2014 with additional sites in 2015 and tree composition in 2015. All soil, needle and leaf samples were analyzed by ICP-OES. Additionally, total C and N were analyzed from organic samples by VarioMax. Rainwater and snow samples were analyzed with ion chromatography at Finnish Meteorological Institute. Based on soil and needle samples we currently formulate a statistical model to explain the relationship between soil nutrient concentrations and needle nutrient concentrations. For ground vegetation we first ordinated the data using the global non-metric multidimensional scaling (NMDS) and then fitted the soil P concentration to ordination pattern of sample plots as smooth surfaces by generalized additive models (GAM). Based on the ordination we found the connection between the soil nutrient concentrations and vegetation cover data. For this reason, continue in building a statistical model on response of ground vegetation cover to soil nutrient concentrations, especially of P.

CONCLUSIONS

We found that the total P concentrations in the soil of most of our sites was within the range of given in the literature (Vance et al. 2003, Jones and Oburger 2011). The sites with lower P concentrations were dominated by pine and spruce and relatively low number of plant species in the ground vegetation. In sites with high soil total P the dominating tree species was birch, and the ground vegetation had higher species number than at the sites with lower soil P. In most cases also other tree species were present at the birch-dominated sites, which made needle sample comparison possible between the sites. We didn’t find differences in the needle P concentrations between different sites, even when the soil concentrations differed. The preliminary results from our statistical model imply that the soil total P is, however, still affecting the needle P concentrations. We will get more detailed results about this during September 2016. *Picea abies* 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).

![Figure 1](image_url)

Figure 1. Research sites (A1-D15) ordinated by their ground vegetation cover with global non-metric multidimensional scaling (NMDS). Soil total P concentrations (red lines) in humus or O layer have been fitted as smooth surfaces by generalized additive models (GAM). Blue arrow points the direction where soil P concentration is increasing. Sites D13, A3 and B6 (on the right-hand side of the picture) are birch-
dominated sites with relatively rich ground vegetation cover. They also have the highest soil total P concentrations in the O layer. Though the statistical models are not complete yet, we can see from our preliminary results that soil total P concentration and ground vegetation cover are connected to each other. Based on the NMDS the sites that have high soil total P in the organic soil layers also have similar type of ground vegetation with each other (Figure 1). They have forbs, such as *Rubus arcticus*, growing on them as well as various graminoid species. The sites where soil total P is lower don’t have forbs growing on them and the graminoid species are limited mainly to *Deschampsia flexuosa*, which grows on almost all sites.

Aerial deposition of P was basically non-existent and other measured inorganic ions had low concentrations as well. Mean air temperature measured at Värriö Research Station has risen notably within the last decades (Figure 2). Mean annual temperature of the last 20 years (1996-2015) was 0.10°C, whereas during the previous 19 years (1977-1995) it was -0.87°C. Warming has been shown to affect vegetation dynamics in the north in many ways. In addition to affecting the ground vegetation and nutrient cycling via changed microbial activity directly (Rustad et al. 2001, Robinson et al. 2002, Sjögersten and Wookey 2004, Hicks Pries et al. 2013), warmer air temperatures may also cause variations in insect populations. Hunter et al. (2014) studied the moth populations of Värriö in relation to changing climate. They noticed that the moths whose larvae feed on living vascular plants reacted more positively to climate change than those whose larvae feed on other plant resources, such as litter and lichen. This type of changes can impact the plant dynamics in subarctic region remarkably. Experimental warming in the low Arctic (Walker et al. 2006) resulted in increased amounts and heights of forbs and graminoids. This together with high soil P could result in great changes in the vegetation cover. On the other hand the same study found that in 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. The changes related to warming seem to be somewhat contradictory and it is difficult to say what the total impact will be.

![Figure 2. Mean annual air temperatures at Värriö Research Station in 1977-2015.](image)

ACKNOWLEDGEMENTS

This work was supported by Maj and Tor Nessling Foundation and Center of Excellence (grant no 272041).
REFERENCES


APPROXIMATE SOLUTIONS FOR OPTIMAL STOMATAL CONDUCTANCE IN STEADY-STATE PHOTOSYNTHESIS MODELS

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Keywords: photosynthesis modelling, analytical solution, steady state, stomatal control.

INTRODUCTION

Theoretical models that couple together the xylem (water transport) and phloem (carbon transport) sides of a tree are developed and analytically solved in an approximate manner. The task is to find the stomatal conductance that maximizes the metabolic rate of the tree. The purpose of this is to enable further testing of the hypothesis that the maximization of this rate would explain the way trees control their stomatal openings.

MODELS

The two steady-state models assume immediate transport and use of photosynthesized products as well as a non-linear relationship between photosynthesis rate and carbon dioxide concentration within the leaf. Evapotranspiration, water and carbon dioxide uptake, incident photochemically active radiation and tree water status are coupled together, which results in an explicit dependence of photosynthesis rate on stomatal conductance. In our steady-state case this rate equals phloem transport and sink sugar utilization rates, so photosynthesis rate represents a more general metabolic rate.

According to our hypothesis, the optimal state for the tree in given environmental conditions can be found by maximizing this metabolic rate with respect to stomatal opening. The non-linear nature of certain relations in the model makes it impossible to find an exact analytical solution to this optimal stomatal opening. By way of some reasonable approximations, an approximate analytical solution can, however, be found for both models. The approximations assume certain specific environmental conditions, yet are sufficiently general to be useful and provide new insight.

The difference between the two models is the specific non-linear dependence of the photosynthesis rate on the internal carbon dioxide concentration of the leaf. The first model uses a simple “Michaelis-Menten-type” saturating function:

\[ A \propto \frac{C_i f_{\text{sat}}}{C_i + f_{\text{sat}}} \]

The second is an application of the widely used “Farquhar-type” mechanistic biochemical photosynthesis model along the lines of Thum et al. (2007), in which the function is defined piecewise. Both of the two functions between which there is a choice in the second model essentially follow the form of a Michaelis-Menten-type function.

RESULTS

The results indicate qualitative agreement with observed phenomena. The first, more simple Michaelis-Menten-type model yields the following approximate optimal stomatal conductance \( g^* \) (for explanation of symbols see Table 1):

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\[ g^* \approx \left(1-\frac{\Psi_{soil}}{\Psi_0}\right) \frac{f_{sat}}{C_a+f_{sat}} \sqrt{-f_{sat} K \Psi_0 1.6 d_w F_{mol_{-}m^3}} \]

Given the dependence on \( C_a \) and \( d_w \), this relates well to the unified stomatal model introduced by Medlyn et al. (2011) and gives a new interpretation to the empirical constants in it.

The approximations are slightly biased towards smaller maximal values of metabolic rate and larger values of optimal stomatal conductance. In a typical case the relative errors are of orders of \( 10^{-3} \) and a few per cent respectively.

The second model with the Farquhar-type photosynthesis rate yields an optimal stomatal conductance of similar form in most cases. Both have the same form with respect to many variables, most notably \( C_a \) and \( d_w \). The biases in this second model are similar, and the relative errors are somewhat larger, yet not unreasonable.

### Table 1. Meanings of symbols.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Psi_{soil} )</td>
<td>soil water potential</td>
</tr>
<tr>
<td>( \Psi_0 )</td>
<td>leaf water potential at which photosynthesis stops due to drought</td>
</tr>
<tr>
<td>( A )</td>
<td>photosynthetic rate</td>
</tr>
<tr>
<td>( C_a )</td>
<td>carbon dioxide concentration of ambient air</td>
</tr>
<tr>
<td>( C_i )</td>
<td>carbon dioxide concentration inside the leaf</td>
</tr>
<tr>
<td>( d_w )</td>
<td>difference in molar fraction of water vapour pressure between the air inside and outside the leaf</td>
</tr>
<tr>
<td>( f )</td>
<td>factor related to intensity of incident photochemically active radiation</td>
</tr>
<tr>
<td>( F_{mol_{-}m^3} )</td>
<td>conversion factor from moles to cubic metres for water</td>
</tr>
<tr>
<td>( f_{sat} )</td>
<td>saturation parameter for Michaelis-Menten curve</td>
</tr>
<tr>
<td>( g^* )</td>
<td>stomatal conductance that maximizes metabolic rate</td>
</tr>
<tr>
<td>( K )</td>
<td>xylem hydraulic conductance from root to leaf</td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENTS

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REFERENCES


WHAT IS THE ROLE OF ICELANDIC DUST IN THE ARCTIC AMPLIFICATION?

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\textsuperscript{2}Department of Physics, University of Helsinki, Finland.

Keywords: SNOW, ALBEDO, MELT, SPECTRAL, REFLECTANCE, VOLCANIC, ICELAND.

INTRODUCTION

Effects on climate of the deposition of light-absorbing particles on snow have been proposed to result from reduced snow albedo and increased melt (Bond et al. 2013). Such effects are usually linked to soot (BC), but in the Arctic region the effects of volcanic ash or dust particles may be important, too. There are over 30 active volcanoes or volcanic systems in Iceland, and seven major dust sources. The properties of ash and dust from these sources show considerable physical and chemical variability.

In our recent paper, we have brought up and hypothesized the cryospheric role of Icelandic dust under the title “Icelandic volcanic dust can have a significant influence on the cryosphere in Greenland and elsewhere” (Meinander et al. Polar Research, 35, 31313, doi:10.3402/polar.v35.31313, 2016). We argue that the assessment of Icelandic dust on snow/ice surface darkening and melt is currently unavailable and therefore scientific research is critically needed. Transport and deposition of light-absorbing Icelandic volcanic dust can have a significant influence on the cryosphere, in Greenland and elsewhere, but it is not included when glacier and ice cap melt rates and deglaciation are investigated. We conclude that more scientific results are critically needed to assess the cryospheric effects of Icelandic dust and ash.

MATERIALS AND METHODS

Within the NCoE CRAICC and the FCoE ATM, our Arctic and Antarctic snow impurity and snow reflectance/albedo and density activities have included both continuous long-term and campaign-based, and the use of various modelling approaches (SILAM for air pollution transport, Libradtran for radiative transfer, SNICAR for snow albedo; more detailed in Meinander et al. 2013). Our long-term data are: a) UV albedo measurements on Arctic seasonal snow at Sodankylä, North Finland, on the operational albedo field of the Arctic Research Station since 2007 during snow time (Meinander et al. 2008); b) UV albedo measurements on Antarctic snow at Marambio since 2013 (Meinander et al. 2014); c) weekly analysis of EC/OC in Sodankylä snow samples (Meinander et al. 2013); and d) ancillary atmospheric and meteorological data of Sodankylä and Marambio (see, e.g., Meinander et al. 2008, 2013, 2014a,b). Our experimental data consist of: a) the Soot on Snow (SoS-2013) experimental data from Sodankylä, where we have measurements on snow albedo and reflectance at 320-2500 nm, induced by artificial deposition of soot, volcanic sand and glaciogenic silt (e.g., Meinander et al. 2014a); b) the data from the SNORTEX campaigns at Sodankylä (Meinander et. al 2013 and 2014), and c) new smaller outdoor and laboratory experiments in Kumpula in 2015 (Dragosics et al. 2015), as well as d) snow sampling from Iceland in March 2016.
CONCLUSIONS

We examined the effects of deposited volcanic ash on ice and snow melt using laboratory and outdoor experiments. These experiments were made in Kumpula, Helsinki, during the snow melt period. Two different ash grain sizes (1 φ and 3.5 φ) from the Eyjafjallajökull 2010 eruption, collected on the glacier, were used. Different amounts of ash were deposited on snow or ice, after which the snow properties and melt were measured. The results show that a thin ash layer increases the snow and ice melt but an ash layer exceeding a certain critical thickness caused insulation (Table 1).

<table>
<thead>
<tr>
<th>Material</th>
<th>Effective thickness [mm]</th>
<th>Critical thickness [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt St Helens (1980) ash</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>Hekla (1947) tephra</td>
<td>2</td>
<td>5.5</td>
</tr>
<tr>
<td>Rock debris</td>
<td>~10</td>
<td>~15-50</td>
</tr>
<tr>
<td>Villarrica tephra</td>
<td>-</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Dust (largely organic matter)</td>
<td>-</td>
<td>1.33</td>
</tr>
<tr>
<td>Eyjafjallajökull ash (2010, 1 φ)</td>
<td>1</td>
<td>9-15</td>
</tr>
<tr>
<td>Eyjafjallajökull ash (2010, 3.5 φ)</td>
<td>≤ 1-2</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 1. Effective and critical thicknesses for different materials such as tephra, rock debris and dust. The effective thickness is the thickness when the material covered ablation is maximized. The critical thickness is the thickness of the material covering the ice or snow where the ablation rate of the material-covered ice or snow equals that of the clean snow or ice; more material will start to insulate. (Dragosics et al. 2016).

ACKNOWLEDGEMENTS

We gratefully acknowledge the Academy of Finland (A4-project, grant no. 254195), the Academy of Finland Centre of Excellence in Atmospheric Science – From Molecular and Biological processes to the Global Climate (ATM) (for years 2014-2019, grant no. 272041), the Nordic NCoE “The Nordic Centre of Excellence Cryosphere-atmosphere interactions in a changing Arctic climate (CRAICC)”, the ATM-DP of University of Helsinki, and the COST SNOW (www.harmosnow.eu).

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DOES INCREASING TEMPERATURE INCREASE CARBONACEOUS AEROSOL DIRECT RADIATIVE EFFECT OVER THE SOUTHEASTERN US AND BOREAL 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). There is conflicting evidence as to whether the aerosol direct effects have a temperature dependence due to increased BVOC emissions.

The main objective of this study is to investigate the causes of the observed effect of increasing temperatures on the aerosol direct radiative effect, and to provide a quantitative estimate of this effect and of the resulting negative feedback in a warming climate. More specifically, we will investigate 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. In addition to BVOCs, SOA formed in aqueous phase and biomass burning emissions could also explain the temperature dependence of aerosol direct radiative effect thus, the contributions of these sources on AOD are analyzed as well.
METHODS

The study is done using a combination of satellite data and climate modelling. Key remote sensing data used are 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 (NO₂), formaldehyde (HCHO) and water vapour, and soil moisture. For the modelling work we are using aerosol-chemistry climate model ECHAM-HAMMOZ, which describes all known relevant atmospheric aerosol processes.

The core data sets for this study are provided by the Advanced Along Track Scanning Radiometer (AATSR) that flew on the ESA polar orbiting Environmental Satellite ENVISAT (2002-2012). We are using AATSR AOD available from the ESA Aerosol CCI project and AATSR LST data from ESA's GlobTemperature project. More specifically, we are using daily Level 3 AOD retrievals done with the ADV algorithm (Kolmonen et al., 2016) from the full mission (2002-2012). The Level 3 data with spatial resolution of 1 × 1 degrees was chosen because it is close to the spatial resolution of climate models. The Level 3 LST data (Prata, 2002) with higher resolution (0.01 × 0.01 degrees) was regridded to 1 × 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 are using ancillary data. Because we are mainly focusing on remote areas of Eurasia, we need to rely on satellite data since ground-based information is very sparse. Here we are using 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 are using Level 3 total column water vapour measurements from the same instrument. Water vapour burden is used in the evaluation of model output and in our analysis of the satellite based AOD-LST relationship. In addition, we are using the following NASA products to support our analysis: NO₂ and HCHO from the Ozone Monitoring Instrument (OMI). NO₂ is used to identify aerosols that are mixed with anthropogenic pollution whereas HCHO can be used as a tracer for SOA originating from biogenic or biomass burning emissions. Daily Level 3 OMI NO₂ and Level 2G HCHO data are available from 2005 onwards. Furthermore, we are using data from ESA's Soil Moisture-CCI. The homogenized and merged soil moisture product provides daily surface soil moisture with a global coverage and a spatial resolution of 0.25°. Soil moisture information is used in the evaluation of model output and in our analysis of the satellite based AOD-LST relationship.

ECHAM-HAMMOZ (version ECHAM6.1-HAM2.2-SALSA) is an aerosol-chemistry climate model developed jointly by the Finnish Meteorological Institute, MPI-MET Hamburg, ETH Zürich, FZ Jülich, Oxford University, and TROPOS Leibniz. The atmospheric circulation model ECHAM solves the fundamental equations for the atmospheric flow, physics and tracer transport. The aerosol model HAM takes advantage of the Sectional Aerosol module for Large Scale Applications (SALSA) which was used to calculate aerosol microphysics (Kokkola et al., 2008; Bergman et al., 2012). SALSA describes the aerosol population consisting of sulphate (SO₄), sea salt, organic carbon (OC), black carbon (BC), and mineral dust, and uses 10 size sections to cover the size range from 3 nm to 10 μm. External mixing of aerosol particles was tracked with 10 additional sections. Anthropogenic and biomass burning aerosol emissions were described with AeroCom-II Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) data (Riahi et al., 2007, 2011).

In our setup of ECHAM-HAMMOZ, organic mass is emitted both as primary organic matter (POM) and in form of volatile organic compounds (VOC). Anthropogenic VOCs simulated are xylene (XYL), toluene (TOL), and benzene (BENZ) and they are entered into the model atmosphere based on emission inventories (Riahi et al., 2007, 2011). On the other hand, biogenic VOC emissions are computed online.
using the biogenic emissions model MEGAN (Model of Emissions of Gases and Aerosols from Nature, Guenther et al., 2006). In the setup presented here, the biogenic VOCs considered are isoprene (ISOP) and monoterpenes (MTP). Once emitted, all anthropogenic and biogenic VOCs are subject to gas-phase oxidation by hydroxyl (OH), ozone (O$_3$) and nitrate (NO$_3$). The concentrations of OH, O$_3$ and NO$_3$ are described with precomputed climatological 3D fields from the MOZART model (Horowitz et al., 2003). The VOC oxidation products are grouped into two groups: the first contains organic compounds that form SOA by gas-to-particle partitioning. The oxidation products are categorized according to their volatility, i.e. equilibrium concentrations, using the volatility basis set (VBS) approach (Donahue et al., 2011). The gas-to-particle partitioning scheme of these products is described by Kokkola et al. (2014). The second group contains the organic compounds that form SOA through aqueous phase chemistry, i.e. in our set-up isoprene epoxydiols (IEPOX) and glyoxals (GLYX).

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).

CONCLUSIONS

Goldstein et al. (2009) detected an exponential dependence between the temperature and AOD in the southeastern US (70-90° W and 30-37.5° N), and hypothesized that it arises from enhanced natural BVOC emissions on warmer days. As a first step in our work, we checked if we were able to detect a similar feature with the AATSR data sets and the climate model. Due to constantly decreasing anthropogenic emissions in this region, our results did not show a clear dependence between temperature and AOD. However, after we used tropospheric NO$_2$ to separate the effect of anthropogenic emissions from the AOD the remaining “non-anthropogenic” AOD increased as temperature increased. Furthermore, the summertime anomalies of the “non-anthropogenic” AOD were positively correlated with the anomalies of HCHO concentrations as Figure 1 shows, which indicates that the source of the temperature dependent AOD over the southeastern US is BVOCs as Goldstein et al. hypothesized. The “non-anthropogenic” contribution increased AOD by approximately 0.009±0.018 K$^{-1}$ while the modelled BVOC emissions increased AOD by 0.022±0.002 K$^{-1}$. Consequently, the regional direct radiative effect (DRE) of the “non-anthropogenic” AOD was -0.43±0.88 W/m$^2$/K and -0.17±0.35 W/m$^2$/K for clear- and all-sky conditions, respectively. The model estimate of the regional clear-sky DRE for biogenic aerosols was also in the same range: -0.86±0.06 W/m$^2$/K.
Figure 1. Summertime anomalies in “non-anthropogenic” aerosol optical depth vs. formaldehyde column over the southeastern US for the years 2005-2011. The “non-anthropogenic” AOD is based on L3 AATSR AOD and OMI tropospheric NO$_2$ observations. HCHO is from L2G OMI observations. The dashed red line represents a linear fit and the error bars represent the uncertainty caused by averaging.

Over the boreal regions the analysis was started with two smaller areas: one over Canada (105-140°W, 55-65°N) and one over Taiga (90-120°E, 50-65°N). Over both areas the observed AOD levels increased as temperature increases. This is illustrated in Figure 2 using monthly averaged values over Taiga. The simulations exhibited similar features over Taiga but not over Canada. The reason for this is currently unclear and it will be studied further.

We assessed the importance of different aerosols sources by comparing the monthly averaged AOD values from the sensitivity simulations with the control simulation as a function of temperature anomalies. This comparison for Taiga is shown in Figure 3. The fractions of biomass burning and biogenic aerosols from
the total AOD are around 15-35 % and these fractions increase as temperature increases. Moreover, both biomass burning and biogenic emissions have comparable effects on the temperature dependency of AOD in this region.

![Figure 3](image_url)

Figure 3. Absolute difference between the monthly AOD averages in the CONTROL simulation and the noBB, noBIOSOA and noAQSOA simulations vs. LST anomaly over Taiga for the summers (JJA) 2002-2010.

The analysis for the boreal forests will be continued with the satellite products to confirm if the biogenic signal in the AOD can be observed. Based on the results over the southeastern US, it is clear that the biogenic contribution to AOD is easily masked by other aerosol sources, such as anthropogenic emissions. Over boreal regions the biogenic signal is weaker than over the southeastern US, thus careful analysis of the satellite products are required in order to get a reliable estimate for the radiative effects of biogenic emissions and for their climatic significance.

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ALTERNATIVE STATISTICAL METHODS TO ANALYSE MASS SPECTROMETER DATA FROM HERBIVORE INDUCED PLANT VOLATILE MEASUREMENTS

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Keywords: SOA, VOC, principal component analysis, discriminant analysis.

INTRODUCTION

Volatile organic compounds (VOC) are constantly emitted from terrestrial plant life. Emissions of plant volatiles are dependent on physiological conditions, and changes in these conditions could rapidly induce emissions or alter emission dynamics. Herbivore induced plant volatiles (HIPVs), are a class of VOCs produced by plants mainly to provide direct and indirect protection against herbivores. In order to study the HIPV formation and the subsequent secondary organic aerosol (SOA) formation and growth an intensive measurement campaign was organized in our research facilities during summer 2015.

DATA AND METHODS

To study HIPV emission dynamics Scots pine saplings were exposed to four bark feeding-pine weevils. The emitting compounds were monitored continuously before and after treatment by proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) and the online measurements were supplemented with cartridge samples, which were analyzed offline via thermodesorption- gas chromatography- mass spectrometry (TD-GC-MS). SOA formation was monitored with High resolution-aerosol mass spectrometer (HR-AMS), and scanning mobility particle sizer (SMPS).

The advanced online monitoring techniques used in this study produce large sets of complex and highly detailed data on the chemical and physical quantities of the emissions. Wyche et al. (2015) used principal component analysis (PCA), hierarchical cluster analysis (HCA) and positive least-squares discriminant analysis (PLS-DA) to address the need for advanced data analysis methodology in the analysis of the large datasets produced in their chamber measurements. Using multivariate statistical methodology to mass spectrometry data is not totally new approach, as positive matrix factorization (PMF), introduced by Paatero and Tapper (1994), is the de facto method for the analysis of AMS measurement data. In addition, Wyche et al. lists several other recent papers using similar methodology for other aerosol composition data. This inspired us to apply similar methodology to our HIPV and SOA formation data.

The data was pre-treated in the same manner as described in Wyche et al., including using Mann-Whitney test to find the signals in individual mass channels which were significantly differing from the signals measured during a blank experiment. The multivariate methods were for the significant signals in order to detect similarities and differentiating patterns between different mass fractions.

Our preliminary results indicate that we can identify different phases of the experiment (pre-treatment, active feeding and post-treatment) with canonical discriminant functions (Fig 1.) by using only 16 of the AMS mass signals.

Figure 2 in turn shows that three out of the four principal components (Factors) pulled out from the PTR-MS data showed significant increase when the bugs started to eat the saplings during the first experiment and one component decreased. It is not yet known which compounds belong to which component. Data for Fig 2. is smoothed for illustrational purposes.
CONCLUSIONS

We applied principal component analysis to AMS and PTR-ToF-MS measurement data in order to separate different chemical compounds from the data. The first PCA results for AMS indicate that the masses can be separated between the components but interpreting the components is still under evaluation. Some shapes in the dividing of the different compounds could be seen and additional analysis is needed to see all significant patterns in the AMS data. PCA is expected to work better for PTR-ToF-MS data as Wyche et al. were able to give clear mapping for gas-phase composition in their analysis. We could detect three or four different principal components out of the PTR-MS data, depending on the measurement, but again, the interpretation of components need substantial amount of work.

The preliminary results showed that pine weevils had a large impact on VOC emissions emitted by Scots pine and subsequent SOA formation. We were able to detect the different phases of the experiments with the multivariate methodology and to construct three or four principal components out of the mass spectrometer measurement data. Subsequent analysis is needed for gaining full insight to the HIPV emission dynamics within our measurement.
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REFERENCES


Seasonal and annual dynamics of VOC emissions from boreal forest soil

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Keywords: VOCs, boreal soil, seasonality, monoterpenes

INTRODUCTION

Boreal forest soil and understorey vegetation contributes to the ecosystem scale fluxes, by emitting or adsorbing diverse range of volatile organic compounds (VOC, for example methanol, acetaldehyde, acetone and isoprenoids etc. isoprene, monoterpenes, and sesquiterpenes). VOCs are important precursors for ozone (O\(_3\)), the hydroxyl radical (OH), and secondary organic aerosol (SOA) formation. The accurate quantification of unknown VOC sources, including soil (Mäki et al., 2016), can improve air chemistry models and reveal currently missing OH sinks (Mogensen et al., 2011). Earlier studies have focused on determining the net exchange of VOCs from forest floor based on manual chamber measurements or small data sets (Hellén et al., 2006; Aaltonen et al., 2011, 2013). Our preliminary results have been analyzed based on the longest continuous data set measured from soils. The measurements were executed in a Boreal Scots pine forest by using three semi-automated chambers connected to the proton-transfer reaction mass-spectrometer (PTR-MS) during the snow-free period from 2010 to 2015. The aim was to determine and quantify diurnal, seasonal and annual dynamics of VOC emissions from boreal forest soil.

METHODS

The measurements were carried out in the southern boreal Scots pine forest at the Station for Measuring Ecosystem-Atmosphere Relations (SMEAR II) in Finland. Soil is Haplic podsol soil where the average thickness of the soil horizons is 6.0 cm (organic layer), 2.0 cm (E-horizon) and 16 cm (B-horizon) (Mäki et al., 2016). VOC fluxes were measured using three dynamic (flow-through) chambers (80 cm \(\times\) 40 cm \(\times\) 25 cm) on permanent stainless-steel soil collars (80 cm \(\times\) 40 cm \(\times\) 10 cm) (Aaltonen et al., 2013). Soil surface inside the collar was covered by the vascular plant species like Vaccinium vitis-idaea L., Vaccinium myrtillus L., Linnaea borealis L., and mosses like Pleurozium schreberi, Dicranum Hedw. sp., Polytrichum Hedw. sp., and Hylocomium splendens Hedw. (Aaltonen et al., 2013). VOC fluxes were analyzed by drawing air samples from the chambers using flow of 1.1 dm\(^3\) min\(^{-1}\), and by directing smaller air sample from the main sample line into a proton-transfer reaction mass-spectrometer (PTR-MS, Ionicon Analytik, Innsbruck, Austria) through the polytetrafluoroethylene (PTFE) tube using flow of 0.1 dm\(^3\) min\(^{-1}\) (Aaltonen et al., 2013). The VOC fluxes of methanol, acetaldehyde, acetone, isoprene, and monoterpenes were calculated based on the linear response of the concentration development during the chamber closure. We quantified forest soil VOC exchange from the snow-free period between in 2010 and 2015.
RESULTS AND DISCUSSION

Forest floor VOC exchange was dominated by monoterpenes (-67.0–435.0 ng m\(^{-2}\) s\(^{-1}\)), methanol (-56.0–182.0 ng m\(^{-2}\) s\(^{-1}\)), and acetone (-69.0–41.0 m\(^{2}\) s\(^{-1}\)). The forest floor was a net source of VOCs when chamber temperature and photosynthetically active radiation increased (Figure 1). VOC sources in forest floor are tree roots, understorey vegetation, and the organic soil layer (Hayward et al., 2001; Hellén et al., 2006; Aaltonen et al., 2011; Greenberg et al., 2012), and temperature regulates VOC synthesis activity, volatilization and diffusive transport.

Our results showed evidence that forest floor emitted water soluble methanol and acetone when photosynthetically active radiation (PAR) and temperature were high, but forest floor became a sink when temperature and PAR decreased (Figure 1b and 1c). The probable sink was the adsorption of methanol and acetone into condensate water films on leaf surfaces during nighttime, when temperature decreased.

![Figure 1. Relationship between monoterpene (a), methanol (b), and acetone (c) fluxes (ng m\(^{-2}\) h\(^{-1}\)) and chamber temperature (°C) with photosynthetically active radiation (µmol m\(^{-2}\) s\(^{-1}\)), presented as combined data of the chamber 10 at the SMEAR II stand from 2010 to 2015.](image-url)
The monthly average monoterpane flux was -0.1–23.0 ng m\(^{-2}\) s\(^{-1}\), and there was a clear seasonal trend in monoterpane fluxes (Figure 2). Our results show that the net exchange of monoterpenes from the forest floor was highest in the fall, when trees drop monoterpane-rich needles from the canopy, and in the spring when forest floor still contains fresh organic matter from the last fall (Figure 2). The spatial and temporal variation within the forest floor was high (Figure 2), and monoterpane flux was higher in chamber 10 where vegetation coverage was lower than in chamber 15 (Figure 2a and 2b).

![Figure 2](image)

Figure 2. Monthly average monoterpane fluxes (ng m\(^{-2}\) s\(^{-1}\)) of (a) chamber 10 and (b) chamber 15, and (c) monthly litterfall (g\(_{DW}\) m\(^{-2}\)) at the SMEAR II stand from 2010 to 2015. Litterfall was not determined in May, 2014. Chamber measurements were executed until the beginning of September in 2011, until the beginning of July in 2013 and from the beginning of May to the end of October in 2014 and 2015.

CONCLUSIONS

Our preliminary results showed that the forest floor VOC exchange was dominated by monoterpenes, methanol, and acetone. The seasonal dynamic of monoterpenes emissions was regulated by monoterpane-rich litter input from the canopy, and the highest monoterpane fluxes were measured in the spring and fall.
Forest floor emitted methanol and acetone when photosynthetically active radiation and temperature were high. The forest floor can also be a sink, when water soluble compounds are adsorbed on the condensate water films on leaf surfaces.

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REFERENCES

OBSERVATION-BASED GLOBAL ANALYSIS OF CONTINENTAL BOUNDARY LAYER NEW PARTICLE FORMATION

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Keywords: AEROSOLS, NEW PARTICLE FORMATION AND GROWTH.

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). Formation of secondary aerosol particles is a major source of atmospheric aerosols (Merikanto et al., 2009), and a subject of active research during the past two decades. Regional events of new particle formation (NPF) have been observed worldwide (Kulmala et al., 2004), but in the literature reports of the seasonality of the NPF related parameters are still rather sparse.

MATERIALS AND METHODS

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

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

RESULTS AND DISCUSSION

Database of the seasonal cycle of parameters related to regional new particle formation at 35 sites worldwide was created. Most of the sites are located in the Northern Hemisphere in Europe and the Arctic area. Regional NPF events were observed at all the sites throughout the year. Average NPF frequencies ranged from 12% of days during December–February to 31% of days in March–May. The smallest NPF frequencies occurred in the polar areas, and the highest in the African savannah area.
Figure 1. The site specific annual averages of formation rate $J_{nuc}$ of nucleation mode particles vs. their growth rate GR.

The particle formation rates do not, on average, show large seasonal variation, but there are large differences between different environments. The highest formation rates that are over 1 cm$^{-3}$ s$^{-1}$ occur inside cities and other anthropogenically heavily influenced areas. In these areas the SO$_2$ concentrations are typically high leading to high concentrations of sulphuric acid, which is one of the key precursor species in atmospheric NPF. On the other hand, the highest particle growth rates do not occur in these same areas of high formation rates, pointing to the decoupling of the mechanisms leading to the initial particle formation and the subsequent growth of the particles.

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REFERENCES


INTRODUCTION

Atmospheric aerosol particles are not distributed uniformly in the atmosphere, their size and composition vary in time and place. These are some of the reasons why aerosols remain one of the largest sources of uncertainties in the climate predictions (IPCC, 2013). Understanding the vertical distribution of aerosols and their optical properties is important for determining the aerosol direct and indirect radiative forcing (Haywood and Ramaswamy, 1998). Lidar measurements are able to show the evolution of aerosol layers with high resolution in space and time. (Wandinger et al, 2011). More detailed information about particles sizes and concentration but with lower spatial resolution can be obtained by in-situ airborne measurements. Therefore, the main objective of this study was to combine airborne and lidar measurements in order to increase understanding of the temporal, vertical and spatial variability of aerosol properties in the lower troposphere.

METHODS AND DATA

A High Spectral Resolution Lidar (HSRL) was deployed in Hyytiälä from March to September 2014 as a part of the US DoE ARM (Atmospheric Radiation Measurement) mobile facility during the BAECC (Biogenic Aerosols – Effects on Cloud and Climate) Campaign. HSRL measures aerosol backscatter and depolarization with 1 second resolution at 532 nm. Airborne campaigns took place in April and September 2014 during the operational time of HSRL. The flight tracks were above Hyytiälä at altitudes below 4 km and at a quite low speed (<200 km/h), which allowed measurements with good temporal and spatial resolution. A Cessna FR172F aircraft was modified to carry instruments including a Scanning Mobility Particle Sizer (SMPS), Optical Particle Sizer (OPS) and a CO2/H2O analyser (LI-COR LI-840). SMPS has a temporal resolution of 10 min and measured particle sizes from 0.1 to 0.23 µm, while OPS has a 10 sec resolution and measuring particle sizes from 0.3 to 9 µm. A schematic measurement set-up can be seen in Fig. 1.

Figure 1. Schematic figure of the measurement setup: high spectral resolution lidar operating continuously in Hyytiälä, with the Cessna airplane, carrying SMPS and OPS, making ascents and descents in the vicinity, within 30 km.
RESULTS

All instruments worked well during a sequence of three days in April from 8th to 10th, thus, this period was chosen for the further analyses. April 9 2014 is one of the case study days. It was a clear sky day with air masses coming from the north and a new particle formation event was detected by ground based measurements at the SMEAR station in Hyytiälä. Two flights were performed by Cessna during this day: from 8 to 10 UTC and from 13 to 14.30 UTC. Figure 2 shows HSRL backscatter cross section from 7 to 10 UTC. Several layers can be seen in Fig. 2: the lowest layer corresponds to a well-mixed boundary layer that reaches from the surface up to 1200 m, then there is a middle layer at 1200-1700 m, followed by an upper layer that stretches from 1800 m to 3000 m. Profiles of LI-COR relative humidity (RH) measurements made on board the aircraft support these layers identification. The highest RH values of 40% is detected at the top of the boundary layer, while a dry layer from 1200 to 1700 m has the lowest values (5-10%). At 1700 m RH starts growing to reach 20% and then stays constant at the upper layer. Radiosonde was launched during the time Cessna was flying and its relative humidity profile is shown in blue on the figure 2. This profile is similar to Cessna and also confirms recognized layers.

Figure 2. To the right, HSRL backscatter cross section from 7.00 to 10.00 on April 9 2014 measured at the same time as Cessna was flying. To the left, relative humidity profiles averaged for Cessna climb (red) and descend (pink) as well as RH profile from a radiosonde (blue) that was launched at 5.30. The well-mixed boundary layer reaches from surface to 1200 m, followed by a dry layer between 1200 and 1700 m, and, finally, a more humid upper layer is situated between 1800 m to 3000 m.

Figure 3 shows aerosol size distributions that were merged together from the measurements of the SMPS and OPS for two flights. The size distributions similar in shape and concentrations were combined into the layers. From three layers in the Figure 3 during both flights the boundary layer had the highest particle concentration in all size ranges. It is interesting to notice that the high concentration of the nucleation mode particles were detected only during the descend of the morning flight. The new particle formation event started while Cessna was flying outside the BL and, thus, small particles were detected only during second part of the flight. During both ascend and descend of the afternoon flight the concentrations of ultrafine particles were already similar and peaked at 20 nm. The middle interface layer was dominated by accumulation mode particles between 0.1 and 0.6 µm during both flights. The lidar usually detects aerosols starting from 0.1 µm, thus stronger scattering is seen for this layer in Figure 2 compared to the upper layer. The upper layer had fewer particles in all size ranges, and no particles smaller than 20 nm were detected during the morning flight. On the other hand, during the afternoon flight some very small particles were observed on several heights of the interface layer and the upper layer. HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model, http://ready.arl.noaa.gov/HYSPLIT.php) backward trajectories were calculated for every 50 m in altitude, and showed that the BL and the upper layer originated from a little bit different locations.
Figure 3. Aerosol size distributions combined into layers according to similarity in shapes and concentrations, measured by airborne SMPS and OPS, for the first and second flights during April 9. The distinguished layers corresponded with the layers observed by the HSRL on fig.2.

CONCLUSIONS

We observed that the highest concentration of aerosols in all size ranges was found predominantly in the BL. The shape of the size distribution in the upper layer was often similar to the BL but with overall lower concentrations due to dilution of particles into a large volume of air. The interface layer, that connects two neighboring layers, combined properties of both layers. Turbulent mixing ensured lower variability in the size distribution in the BL on short timescales and more variability in the free troposphere. 96-hours back trajectories for every 50 m for the altitudes from 0 to 4 km m.s.l. showed difference in the origin of the air masses. Origin of the air masses, as well as mixing and deposition, affect aerosol size distribution in different layers.

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REFERENCES


EFFECTS OF RADIATION TRANSMITTANCE THROUGH CLOUDS ON GROSS PRIMARY PRODUCTION

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Keywords: GROSS PRIMARY PRODUCTION, CLIMATE FEEDBACK, AEROSOL-CLOUD INTERACTIONS.

INTRODUCTION

Temperature driven increases in emissions of biogenic organic compounds have been shown to exert a negative (i.e. cooling) aerosol-climate feedback, due to enhanced condensation growth of aerosol particles, which increases the cloud condensation nuclei (CCN) formation (Kulmala et al., 2004; Paasonen et al., 2013). Increasing concentrations of CCN increase the cloud albedo and lifetime, which decreases the total amount of solar radiation reaching the Earth’s surface. However, in addition to cooling the surface, the decreased radiation level can be presumed to decrease the CO₂ uptake in photosynthesis, thus increasing the atmospheric CO₂ concentration and producing an opposite effect, partly mitigating the initial negative feedback (Figure 1).

In this study we inspect the level of variation in gross primary production (GPP) arising from changes in transmittance of radiation through clouds. We intend to continue this research by estimating the long-term warming effect of CO₂ remaining in global atmosphere, due to changes in radiation transmittance arising from increasing aerosol concentrations. In the end, we aim for a quantified comparison of this positive feedback and the above-explained negative feedback in terms of Earth’s radiation budget. This analysis will provide a novel piece in the research of the effects of climate change on the carbon cycle, where the extreme events have been previously underlined (e.g. Reichstein et al., 2013).

METHODS

For our analysis, we inspect data from seven measurement sites in varying vegetation zones and land-use areas around the world. The sites are listed in Table 1. From each site, we apply GPP data calculated from
CO₂-flux measurements and the measured global radiation levels. Additionally, we calculate the hourly values for maximum clear sky radiation for each measurement site, and inspect only the data during non-clear sky conditions. This is determined by choosing the data during which the radiation transmittance, describing the ratio of observed and maximum radiation, is below 0.7. With these data, we inspect how the ratio of momentary GPP to the maximum GPP during the following clear sky days responds to the radiation transmittance.

Our next goal is to inspect how the estimated decrease in radiation transmittance affects the amount of CO₂ remaining in the air. This will be calculated by considering the change in ecosystem respiration subsequent to the change in carbon uptake. In practice, the effect of altered GPP on atmospheric CO₂ concentration will be determined based on the turnover times, which describe the delayed changes in ecosystem respiration arising from the changes in GPP (Carvalhais et al., 2014).

Finally, we will determine how large areas of the global domain the GPP can be considered to be uniformly affected by the changes in radiation transmission. With this information we calculate the additional amount of CO₂ remaining in the atmosphere due to increased cloud albedo, which is estimated to be directly related to radiation transmittance during non-clear sky conditions. We compare the long-term warming effect of this additional CO₂ concentration with the cooling effect originating from the same increase of cloud albedo.

<table>
<thead>
<tr>
<th>Site</th>
<th>Country</th>
<th>Vegetation</th>
<th>Lat., long.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyytiälä</td>
<td>Finland</td>
<td>Conif. Forest</td>
<td>62N, 24E</td>
<td>Suni et al., 2003</td>
</tr>
<tr>
<td>Changleing</td>
<td>China</td>
<td>Grassland</td>
<td>44N, 126E</td>
<td>Dong et al., 2011</td>
</tr>
<tr>
<td>Klingenberg</td>
<td>Germany</td>
<td>Crop land</td>
<td>51N, 14E</td>
<td>Owen et al., 2007</td>
</tr>
<tr>
<td>Mongo</td>
<td>Zambia</td>
<td>Savannah</td>
<td>15S, 23E</td>
<td>Merbold et al., 2011</td>
</tr>
<tr>
<td>Amazon</td>
<td>Brazil</td>
<td>Tropical forest</td>
<td>3S, 55W</td>
<td>Saleska et al., 2003</td>
</tr>
<tr>
<td>Tumbarumba</td>
<td>Australia</td>
<td>Eucalyptus forest</td>
<td>36S, 148E</td>
<td>Leuning et al., 2005</td>
</tr>
</tbody>
</table>

Table 1. Description of the measurement sites for the applied data.

RESULTS

In Figure 2 we present the impact of radiation transmittance on GPP, the latter being depicted as the ratio of the momentary observed GPP and the maximum GPP during the upcoming 6 days at the inspected hour of the day. The reason for choosing the approach of 6 upcoming days for the determination of the seasonal maximum is mainly in the data set from agricultural area of Klingenberg, where the harvesting was found to effectively alter GPP. This effect hindered the relation between GPP and radiation transmittance, if the seasonal cycle was not determined with rather short period of upcoming days. On the other hand, different approaches tested did not significantly alter the figures for other sites.

Figure 2 shows rather similar relative changes in GPP as a function of radiation transmittance in most of the sites, excluding the Tumba Rumba site in Australian Eucalyptus forest. In all the other sites, when the transmittance starts decreasing from 0.7, the GPP starts decreasing as well, but this decrease becomes steeper when the transmittance goes roughly below 0.4. It should be later on still inspected, whether the transmittance values of close to 0.7 can always be attributed to clouds shading the direct sunlight, or can, e.g. in Amazonas, this transmittance be connected to a heavy biomass burning episode. The different behaviour of GPP at the Eucalyptus forest, where GPP decreases in a strictly linear manner as a function of transmittance, is an interesting exception. Even with this exception, we can estimate that in most vegetated areas around the world, the decrease of GPP due to clouds dimming the solar radiation can be studied as an uniform phenomenon.
Figure 2. The ratio of hourly GPP values normalized with the maximum GPP during the upcoming 6 days at the same hour of the day as a function of radiation transmittance. The data considered as cloudy conditions is to the left of vertical lines, indicating radiation transmittance of 0.7.

NEXT STEPS

The next part of the study will be to apply a process model to determine the effect of altered ecosystem carbon uptake via GPP (here due to a change in radiation transmittance) on the ecosystem respiration, which would take place only after the long carbon turnover time, as described by Carvalhais et al. (2014). Then we will determine, how much the changes in GPP affect the atmospheric CO$_2$ concentrations, when the subsequent effect on respiration is taken into account. When these calculations are finished, we will compare the radiative forcing caused by the altered CO$_2$ concentration with the original forcing caused by the change in transmittance (Paasonen et al., 2013). In this comparison, the change in transmittance needs to be considered as a permanent, in order to be able to compare these effects of very different time scales. However, with this analysis we will make at least an order of magnitude estimate of the relative radiative forcings of these two sides of the aerosol-cloud-climate feedback mechanism.
ACKNOWLEDGEMENTS

This study was supported by Academy of Finland Centre of Excellence program (project no. 272041). This work used eddy covariance data acquired and shared by the FLUXNET community, including these networks: AmeriFlux, AfriFlux, AsiaFlux, CarboAfrica, CarboEuropeIP, CarboItaly, CarboMont, ChinaFlux, Fluxnet-Canada, GreenGrass, ICOS, KoFlux, LBA, NECC, OzFlux-TERN, TCOS-Siberia, and USCCC. The FLUXNET eddy covariance data processing and harmonization was carried out by the ICOS Ecosystem Thematic Center, AmeriFlux Management Project and Fluxdata project of FLUXNET, with the support of CDIAC, and the OzFlux, ChinaFlux and AsiaFlux offices.

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CLOUD AND WET PROCESSING OF α-PINENE SOA PARTICLES AFFECT THEIR RH-DEPENDENT PHASE STATE BEHAVIOUR

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Keywords: SOA, PHASE STATE, PHASE TRANSITION, CLOUD ACTIVATION.

INTRODUCTION

Atmospheric submicron organic aerosols have major contribution to aerosol-radiation interaction and cloud formation. Secondary organic aerosol (SOA) particles formed via ozonolysis of α-pinene are commonly used to simulate atmospheric organic aerosols in laboratory conditions. At room temperature (T), α-pinene SOA particles derived from ozonolysis have been shown to undergo phase transition from semisolid/solid to liquid as relative humidity (RH) is increased from ~60% to >90% (Pajunoja et al. 2015). While in certain warm summer conditions, ambient SOA measurements have indicated lower liquefying RH ranges (Bateman et al. 2016, Pajunoja et al. 2016), in boreal environmental conditions the ambient observations have shown organic-dominated SOA particles to be in highly viscous phase at RH < 30% (Virtanen et al. 2010). The effect of phase state of SOA particles on their behaviour in the atmosphere has recently been under investigations. During transport of atmospheric SOA particles from the lower troposphere to the upper troposphere where cloud formation typically occurs, RH and especially temperature may be significantly different than for ground level measurements. Such variations in surrounding conditions can induce changes in phase state and morphology of the SOA particles, which in turn both influence and are influenced by the particles’ chemical properties. Moreover, changes in particle-phase water concentration may trigger chemical reactions in the particles leading to changes in composition of dry particle mass. In this study, we investigate how cloud and wet processing of α-pinene SOA particles affect their phase state and exceptionally wide temperature and RH ranges were combined with cloud activations experiments.

METHODS

To simulate updraft of SOA particles in the atmosphere and investigate the influence of atmospherically relevant conditions (T and RH) on their phase state, morphology, chemical composition, and cloud activation, we used two chambers at the Karlsruhe Institute of Technology (KIT). α-pinene SOA was generated by ozonolysis in a smaller stainless steel NAUA chamber (4 m² stainless steel) at room T to replicate atmospheric ground level SOA formation process. Then the particles were transported into the T-controlled (cooled) AIDA chamber (84 m³, aluminium) where the measurements were done at fixed T between 298 and 208 K. In all measurements, RH in the AIDA was gradually increased at constant T from ~30% to ~95% to enable droplet (ice) activation during a further adiabatic expansion. Phase transitions of the dried SOA particles (mobility diameter 80 – 120 nm) with RH was investigated by the Aerosol Bounce Instrument (ABI, Pajunoja et al. 2015) by scanning RH between ~10% and ~90%. The RH scans were performed at dry AIDA conditions and also just before and after the cloud formation. ABI measurements were conducted at room T and also at equal to AIDA chamber T. The composition of the SOA particles and their surrounding gas phase was measured with an Aerosol Mass Spectrometer (AMS) and a Chemical Ionization Mass Spectrometer with a Filter Inlet for Gases and Aerosols (FIGAERO-CIMS, Lopez-Hilfiger et al. 2014).
CONCLUSIONS

According to ABI measurements, α-pinene SOA particles stay semisolid/solid at dry conditions (RH < 20%) regardless of the history of the particles (i.e. dry, RH cycled, or cloud processed). However, phase transition RH where the actual particle bounce starts to decline, changed during the cloud or wet processing of particles when the temperature was close to room $T$. According to our results, the dried α-pinene SOA particles liquefy at 10 – 15% lower RHs compared to the measurements conducted before RH elevation. This change is irreversible and is not affected by chemical aging of the particles. By decreasing the AIDA temperature substantially, the effect of cloud process or high RH on phase transitions vanishes. The difference in phase transition curves gradually decreases with decreasing AIDA $T$. These results are supported by FIGAERO measurements which show differences in chemical composition for the SOA particles under different temperature and humidity conditions. These results indicate, that, depending on surrounding temperature, the wet and cloud processing of α-pinene SOA particles changes their composition and also affects their phase state.

ACKNOWLEDGEMENTS

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REFERENCES


ROLE OF SURFACE STRUCTURE IN HETEROGENEOUS NUCLEATION OF ICE

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Keywords: ICE NUCLEATION, SIMULATION, MOLECULAR DYNAMICS.

INTRODUCTION

An accurate description of clouds in climate models requires solid knowledge about their properties, but formation of ice clouds, in particular, is not well understood. Substances like water do not necessarily freeze when cooled below their thermodynamic freezing point, as the first steps of crystal formation are energetically disfavoured. Crystallization can only proceed once a crystal of critical size has spontaneously formed in the supercooled liquid. The crystal formation barrier is caused by a competition of bulk free energy difference between the phases, favouring the crystalline phase, and an unfavourable component from interfacial energy between the phases. Ice crystals may form in the atmosphere either by homogeneous or heterogeneous ice nucleation. The latter process, where ice formation is initiated by an aerosol seed particle, is active at clearly higher temperatures than homogeneous nucleation. The effect is not thoroughly understood. Different nucleation modes (immersion-, contact- and deposition nucleation) are active in the atmosphere at different temperature and water supersaturation ranges.

METHODS

We have developed an atomistic model of ice crystal formation using a continuum of methods from density functional theory (DFT) to large-scale classical molecular dynamics (MD). We are looking at kinetic and thermodynamic factors controlling nucleation at different conditions and in the presence of different surfaces with varying lattice match with ice, representing aerosol particles.

To capture the details of the rare stochastic events of ice nucleation, it is necessary to simulate relatively large systems over long time scales, and therefore classical interaction potentials are used. We utilize the TIP4P/2005 model for water (Abascal and Vega, 2005), as this rigid point charge all-atom model has been shown to reproduce the water phase diagram well and is widely used to study water-ice phase transitions, as well as a computationally cheaper monatomic water model (Molinero and Moore, 2009). Unbiased MD is an ideal method to study 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 AgI that are experimentally found to be active in heterogeneous nucleation, and we show what factors are affecting the nucleation activity.

In addition to studying nucleation dynamics with MD, we are looking at accurate energetics and parameterizing classical interaction potentials between water molecules and surfaces with quantum chemical DFT, utilizing the ORCA code (Neese, 2012) with BP86 functional with D3BJ dispersion. Comparison of water layer adsorption on SiO₂ and graphite versus on K-feldspar is helping us understand the difference in nucleation activity between these materials. We are also utilizing DFT simulations to study water adsorption on hydroxylated graphene, a model for weathered black carbon.
CONCLUSIONS

Interaction with a flat surface induces layering in water, the first step towards ice nucleation. 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 (see Fig. 1.) show that surface geometry alone can explain the high nucleation activity of AgI, whereas K-feldspar, which is considered one of the most important ice nucleation agents in the atmosphere, shows very weak activity in mW simulations, without considering the real surface chemistry or defects of the material. Contact nucleation mode simulations show nucleation activity at higher temperatures than immersion, in agreement with experiments. Deposition nucleation mode (i.e. formation of ice from the vapour phase, active at low temperatures in high-level clouds) leads to even more effective creation of hexagonal bilayers on moderately hydrophilic surfaces. This can be attributed to clearly larger diffusivity of water molecules in the building water layers, compared to bulk water in immersion nucleation.

Figure 1. Surfaces with a good lattice match with hexagonal ice nucleate ice effectively in MD. This result with the monatomic water (mW) potential shows that the high nucleation activity of AgI can be explained by surface geometry alone, without considering specific surface chemistry of the material, whereas for K-feldspar the experimentally observed activity is due to other factors. The inset on the right side of the figure shows the surface geometries of the studied surfaces.

ACKNOWLEDGEMENTS

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REFERENCES

HOW A PATHOGENIC FUNGUS BREAKS TREE RESISTANCE?

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Keywords: ENDOCONIDIOPHORA POLONICA, PICEA ABIES, WATER TRANSPORT, SURFACE TENSION, RESIN.

INTRODUCTION

Endoconidiophora polonica (Ascomycota) is a pathogenic blue stain fungus vectored mainly by the spruce bark beetle (Ips typographus), an aggressive forest pest species causing economic losses in forest industry in Europe. Endoconidiophora polonica is a relatively common fungus in European forests, where its major host is Norway spruce (Picea abies L.). Elsewhere I. typographus also infests other Picea and occasionally other conifers. Climate change likely decreases tree vitality e.g. by more frequent storm damages in boreal forests and thus predisposes spruces to this and other 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 (e.g. Jactel et al., 2012). Though both the fungus and tree water transport have been much studied (e.g. Paine et al., 1997; Desperez-Loustau et al., 2006; Meinzer et al., 2001), the physiological mechanism behind the tree weakening process remains unknown. Linking the fungal infection to the 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. This knowledge is also useful in tree breeding and can therefore aid even the forest industry.

There are two hypotheses how E. polonica may hinder the water transport in trees. First, it may grow its mycelium into the tracheids and other conduits, and block mechanically the water transport route through xylem (e.g. Yadeta and Thomma, 2014). However, under microscope such conduits full of hyphae have not been found. It has also been suggested that the mechanical blockage could be due to resinous compounds produced by the tree in response to the infection (Kuroda, 2005). Second, fungus may decrease the surface tension of water inside a tree, which increases the vulnerability of tree water transport to hydraulic disturbances through breaking of the water columns, i.e. by cavitation leading to embolism formation (Tyree and Sperry, 1989). The fungus might itself produce surfactants to decrease the surface tension of transported water, or it might modify the compounds produced by the plants. It is known that E. polonica induces a strong defense reaction in the xylem and phloem (Zhao et al., 2011), and can modify the defense compounds to its own use (Wadke et al., 2016). The fungus may also cause ample oleoresin flow from stems and branches once infecting a living tree (Christiansen, 1985; Kuroda, 2005). This is a defense reaction as well, as the flowing oleoresin is antifungal and also mechanically removes fungal spores (Langenheim, 1994, Hofstetter, 2005).

We set up an experiment to determine which physiological mechanisms are used by infectious strain of E. polonica to overcome the defense mechanisms of Norway spruce. A strain of E. polonica isolated during our previous study in an I. typographus outbreak region in Finland was used in this study. We monitored tree water relations, resin pressure, volatile emissions and tree vigor. Moreover, stem tissue samples were collected to analyze microscopically the fungal succession.
METHODS

The study was conducted at the Viikki campus greenhouses to regulate the prevailing environmental conditions. The cloned saplings of Norway spruce were potted and brought in in May 2016. We used two clones (E1510 and E64) from the Nursery of Natural Resources Institute Finland to study the genetic differences in tree resistance. 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 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 seedling 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 that were carried out with a capillary rise method using the setup of Vanhanen et al. (2008). Also the relative water content was measured from a separate stem piece. The material for chemical analysis was collected with the tree samplings.

Resin pressure in the stems was measured first, in order to observe the constitutive and inducible defense reactions provoked by the inoculations and secondly, to examine the effect of decreasing water potential, hydraulic conductance and conductivity on the resin dynamics. To do this, lightweight differential pressure sensors (Model MPX5250, NXP Semiconductors, Eindhoven, Netherlands, Fig. 1), which were

Figure 1. A sapling with oleoresin pressure meter (in the upper part of the figure), inoculation area (in the middle) and a stem enclosure (in the lower part of the figure). The brownish-coloured declined branches are visible near the infection area.
tailored for this study 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 AND DISCUSSION

The experimental part of the study ended in the end of August 2016. Thus, the results are still partly waiting to be analyzed. However, the preliminary results show that at least the hydraulic conductivity in the infected seedlings was significantly lower than in the control trees (Fig. 2). Also the surface tension seems to be lowered in the infected trees but as the analysis is still ongoing the final results will show if the difference is significant. The hydraulic conductance, that was the relation of tree transpiration and water potential, was not different between the treatments. This imply the cause of disturbed water transport to lay in the lowered surface tension. 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.

Oleoresin pressure followed an expected diurnal pattern throughout the experiment, being high in mid-day and decreasing towards night. During the days directly after the infection, no instant responses in oleoresin pressure were seen. Approximately four weeks after the inoculation, the oleoresin pressures in the infected trees had generally larger daily ranges than in the wounded controls. Whether there are trends in oleoresin pressures in response to the water transport capacity of the trees remains to be analyzed. VOC samples did not reveal any specific compound that would be related to fungus infection. However, monoterpene emission pattern changed over the summer in both wounded and infected trees.
CONCLUSIONS

These results suggest that the mechanism how *E. polonica* overcomes the defense system of *P. abies* are more related to water transport than chemical defenses such as volatile compounds. The details, however, need more analysis.

REFERENCES


FORMATION OF HIGHLY OXIDIZED MULTIFUNCTIONAL COMPOUNDS IN
THE OXIDATION OF ALPHA-PINENE UNDER DIFFERENT
ENVIRONMENTAL CONDITIONS: DIFFERENT PRODUCT PROPERTIES
AND YIELDS

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Keywords: Secondary organic aerosol, Volatile Organic Compounds, Oxidation, PMF.

INTRODUCTION

All around the globe, organic compounds make up a large part of the atmospheric aerosol (Zhang et al., 2007). This organic matter largely originates from the conversion of Volatile Organic Compounds (VOCs) to less volatile forms through oxidation reactions. The formed compounds can then condense to form Secondary Organic Aerosol (SOA) (Zhang et al., 2007). The conversion of VOCs to SOA has been studied extensively over the past decades. Yet still, no comprehensive description of it exists yet. There has been a mismatch between the formation of SOA observed in the atmosphere and that predicted by the models (Hallquist et al., 2009). Only recently, it was discovered that the oxidation of monoterpenes, a dominant group of VOCs emitted from the boreal forests, efficiently forms so called Highly Oxidized Multifunctional organic compounds (HOMs), in yields high enough to possibly explain the discrepancy between measurements and models (Ehn et al., 2014). HOMs are assumed to form through autoxidation of monoterpenes. This autoxidation process can be altered by the presence of different radicals, e.g. nitrogen oxides. To unravel the formation mechanisms of HOMs, we participated in a measurement campaign in the Pacific Northwest National Laboratory (PNNL) in Washington State, USA, where we measured the oxidation of α-pinene, a dominant monoterpene, under different environmental conditions.

METHODS

α-pinene was oxidized under different conditions in a 10 m³ environmental chamber constructed of teflon. Different conditions included the initiation of oxidation reactions by either ozone, hydroxyl radical, or nitrate radical. In addition to varying the initiation reaction, we varied the contributions of different termination pathways of the RO₂ radicals formed in the reactions. The termination pathways varied included the reactions of RO₂ radicals with other RO₂ radicals, with nitrogen monoxide (NO) and hydroperoxyl radical (HO₂). We measured both the gas and particle phase with a wide suite of instrumentation, both from the University of Helsinki and other institutions. The chamber was operated in a continuous flow mode, with a residence time of three hours. We used seed particles, consisting of ammonium sulfate, to promote SOA formation. Both UV and visible lights were controlled to alter the photochemistry in the chamber.

For the measurement of the concentrations and molecular compositions of different HOMs, we used a nitrate ion Chemical Ionization Atmospheric Pressure interface Time-Of-Flight mass spectrometer.
We also measured the concentrations of reactant monoterpenes and concentration of formed aerosol mass, along with measurements of the aerosol size distribution, the volatility of the resulting particles and their activity as cloud condensation nuclei (CCN).

To separate the pathways forming different types of HOMs, we utilized positive matrix factorization (PMF, Paatero and Tapper, 1994). PMF is a technique for separating compounds of different origins, optimized for environmental observations. Here the different origins of the HOMs are different formation pathways, i.e. the initiation of the oxidation reactions by different oxidants, as well as termination of them by different means. An additional constraint that the PMF has is that both the factor profiles and time series are required to be non-negative: this holds true, as concentrations of HOMs are always positive, or zero at minimum.

RESULTS AND CONCLUSIONS

PMF proved a valuable tool for the analysis of the data: using it, we were able to separate the contributions of e.g. different oxidants, and some termination pathways. With addition of nitrogen oxides, we observed a shift to HOMs containing nitrogen, presumably organonitrates. Additionally, the yield of HOMs seemed to increase with the addition of nitrogen oxides. We expect that with further analysis, we will be able to describe the formation of HOMs in more detail still.

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REFERENCES


DAYTIME EMISSION AND NIGHT-TIME UPTAKE CHARACTERIZE CO FLUXES FROM AN AGRICULTURAL BIOENERGY CROP

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Keywords: CARBON MONOXIDE, FLUXES, EDDY COVARIANCE, EMISSION, UPTAKE.

INTRODUCTION

Carbon monoxide (CO) in the atmosphere participates in the chemical reactions with hydroxyl radicals (OH), potentially leading to the production of ozone (O₃), and decreasing the capacity to oxidize atmospheric methane (CH₄). Burning of fossil fuel and biomass and photochemical oxidation of CH₄ and non-methane hydrocarbons are the main sources of CO (Duncan et al., 2007), while the reaction with OH is the major sink for CO in the atmosphere (Duncan and Logan, 2008). Soils are generally considered as a sink for CO due to CO oxidizing bacteria, while production of CO in soils has mostly been related to abiotic processes such as thermal, UV- or visible light-induced degradation of organic matter or plant material (Conrad and Seiler, 1985; Tarr et al., 1995; Lee et al., 2012). Formation of CO in living green plants was found already in the late 1950’s (Wilks 1959), however, the importance of biological CO forming processes in the net CO exchange still remain largely unknown (King and Crosby, 2002).

Most of the reported CO flux measurements are either short-term field experiments, or laboratory incubations with specific treatments of the soil or plant material. Both CO uptake and emissions are reported from soil-plant systems in different climatic regions, however, the high variation between CO uptake and emission rates does not allow yet to classify the ecosystem types or climatic regions.

To our understanding, this is the first study to report long-term and continuous field measurements of CO fluxes (F_{CO}) using the micrometeorological eddy covariance (EC) method. We measured F_{CO} above a boreal perennial grassland ecosystem, reed canary grass, over a 7-month snow-free period in 2011 by two parallel laser absorption spectrometers. We compared the F_{CO} with simultaneously measured fluxes of carbon dioxide (CO₂), net ecosystem exchange of CO₂ (NEE), nitrous oxide (N₂O), heat and energy as well as with relevant soil, plant and meteorological variables. Here we report the seasonal and diurnal variability in F_{CO}, the main abiotic and biotic drivers of F_{CO}.

METHODS

The measurements were conducted on a mineral agricultural field located in Eastern Finland (63°9'48.69" N, 27°14'3.29" E), cultivated with a perennial reed canary grass (RCG, Phalaris arundinacea, L. cv. Palaton). The measurements covered a period from snow-melt to the new snowfall, from April to
November 2011. The crop from the previous season was kept at the site over the winter and was harvested on 28 April (day 118) (Lind et al., 2016). The spring and early summer (days 118-160) was characterized by fast growing crop with the crop height increasing from about 10 cm in mid-May to 1.7 m in late June (day 180), reaching the maximum height of 1.9 m in early July.

The EC measurements of CO and N\(_2\)O fluxes were made as a part of the ICOS (Integrated Carbon Observation System) Finland program by two continuous-wave quantum cascade lasers: AR-CW-QCL (model CW-TILDAS-CS Aerodyne Research Inc., see e.g. Zahniser et al., 2009) and LGR-CW-QCL (model N2O/CO-23d, Los Gatos Research Inc., see e.g. Provencal et al., 2005). CO\(_2\) and H\(_2\)O fluxes were measured by an infrared gas analyzer (LI7000 – Li-Cor Inc., Lincoln, NE, USA) connected to a sonic anemometer (R3-50, Gill Solent Ltd., UK). A weather station monitored continuously several meteorological and soil parameters such as air temperature (T\(_{air}\)) and relative humidity (RH) (model: HMP45C, Vaisala Inc.), precipitation (P\(_r\)) (model: 52203, R.M. Young Company), global (R\(_{glob}\)) and net radiation (R\(_{net}\)) (model: CNR1, Kipp&Zonen B.V.), photosynthetically active radiation (PAR, model: SKP215, Skye instruments Ltd.), soil heat flux at 7.5 cm depth (G) (model: HPF01SC, Hukseflux), soil temperatures at 2.5 cm depth (T\(_{soil}\)) (model: 107, Campbell Scientific Inc.), and soil water content at 2.5 cm depth (SWC) (model: CS616, Campbell Scientific Inc.). All meteorological data were recorded as 30 min mean values and stored using a datalogger (model: CR 3000, Campbell Scientific Inc.). The EC data processing was performed with post-processing software EddyUH (Mammarella et al., 2016).

To evaluate in detail, the seasonal changes in F\(_{CO}\) and factors affecting the fluxes, the data was divided into six periods (days 110-145 (20 April – 25 May) = spring (S), days 146-160 (25 May – 9 June) = early summer (ES), days 205-240 (24 July – 28 August) = late summer (LS), days 241-295 (29 August – 23 October) = autumn (A), and days 296-325 (24 October – 21 November) = late autumn (LA)). To compare diurnal changes in the F\(_{CO}\), the data was further divided into daytime (F\(_{CO, day}\)) and night-time (F\(_{CO, night}\)) data based on sun elevation angle h>0 for daytime and h<0 for night-time, respectively. Pearson correlations between daytime and night-time half-hour average fluxes and other measured parameters were determined. Data processing was performed with Matlab version R2014a (The MathWorks, Inc., United States) and the statistical testing with IBM SPSS statistics 23 (IBM Corporation, United States).

RESULTS

The RCG field was a net source of CO from mid-April in the spring to mid-June (days 110-160), after which the site turned to a net sink until the end of the measurement period in November 2011 (days 161-325). Cumulative CO flux (cum F\(_{CO}\)) curves, calculated by cumulating the half-hourly fluxes, show that the site was a net sink of CO over the 7-month measurement period. During daytime, the net CO fluxes (F\(_{CO, day}\)) were positive during the spring and early summer (days 110-160) and again during late summer (days 205-240). These daytime emissions were highest during the spring. Night-time CO fluxes (F\(_{CO, night}\)) were negative (CO uptake) throughout the whole measurement period with a trend of increasing CO consumption towards late autumn.

The F\(_{CO}\) had a distinct diurnal pattern with an uptake at night and an emission during the day with maximum emissions at noon (Fig. 1). This pattern was most pronounced during the spring, days 110-145, when the maximum daytime CO emissions reached 2.7 nmol m\(^{-2}\) s\(^{-1}\) (Fig. 1). Night-time F\(_{CO}\) show a near constant uptake of CO with a mean of -0.77 nmol m\(^{-2}\) s\(^{-1}\) over the whole measurement period. The diurnal F\(_{CO}\) followed closely the daily pattern of global radiation, R\(_{glob}\) (Fig. 1). The highest radiation intensity was reached during the early summer (days 146-160), while the maximum F\(_{CO}\) were observed during the spring (days 110-145). Compared to the F\(_{CO}\), the diurnal variation in CO\(_2\) exchange, expressed here as net ecosystem exchange (NEE), was very small during the spring (days 110-145) (Fig. 1). A rapid increase in leaf area index (data not shown) during early summer lead to an increase in daytime CO\(_2\) uptake, which is seen in the diurnal pattern with high CO\(_2\) uptake (negative NEE) during daytime and a small positive NEE
during the night (Fig. 1). Maximum NEE values were reached during mid-June (days 161-181) after which the NEE slowly decreased and the CO₂ uptake disappeared by mid-October (day 290).

The most pronounced relationships between F_{CO} and other measured scalars were found for the daytime data (sun elevation h>0) during the spring and early summer. The strongest correlations were found during the spring between F_{CO, day} and R_{glob} (r=0.760, p<0.01), R_{net} (r=0.760, p<0.01), sensible heat flux (H) (r=0.729, p<0.01) and G (r=0.575, p<0.01). These positive correlations remained significant but became weaker towards the end of the measurement period. Strong negative correlations were found during the spring between F_{CO, day} and RH (r=-0.537, p<0.01), and during the early summer with NEE (r=-0.469, p<0.01), while the correlation between daytime F_{CO} and CO concentration (M_{CO}), F_{N2O} or ecosystem respiration (RESP) were very weak throughout the 7-month measurement period F_{CO, night} correlated weakly with F_{N2O} (r=-0.336, p<0.01), H (r=0.315, p<0.01), and LE (r=-0.241, p<0.05) in the spring and with SWC (r=-0.308, p<0.01) during early summer. A strong negative correlation was found between F_{CO, night} and F_{N2O} during mid-summer (r=-0.607, p<0.01) and late autumn (r=-0.514, p<0.01), and a positive correlation between F_{CO, night} and LE (r=0.459, p<0.05) during mid-summer.

![Diurnal cycle of half-hour mean CO fluxes (F_{CO}, nmol m^{-2} s^{-1}), half-hour mean global radiation (R_{glob}, W m^{-2}), and half-hour mean net ecosystem exchange of CO_{2} (NEE, µmol CO_{2} m^{-2} s^{-1}) from the reed canary grass crop from the spring (S, days 110-145) and early summer (ES, days 146-160) periods in 2011. Grey areas indicate the moment of sunrise and sunset, and the vertical bars indicate ±1 standard deviation of the fluxes.](image-url)
DISCUSSION

Based on the 7-month EC flux measurements at the RCG crop, we demonstrate that the EC method is suitable for measuring CO fluxes ($F_{CO}$) from a perennial agricultural crop. We show that the soil-plant system acted as a net source of CO during the spring and early summer and a net sink for CO over the late summer and autumn (data not shown), and that the $F_{CO}$ had a clear diurnal pattern with net CO emissions during daytime and net CO uptake during the night. This source-sink pattern existed over the whole measurement period with decreasing net emissions towards the end of the autumn. To our knowledge, similar long-term and continuous $F_{CO}$ data series measured by the EC method over any ecosystem type does not exist, and hence this study is unique in bringing new insight to the understanding of short-term diurnal and long-term seasonal $F_{CO}$ dynamics at ecosystem-level.

Similar to our study, soils from boreal to tropical regions have been found to have a diurnal pattern with emissions in the noon and uptake during the night (Conrad and Seiler, 1985; Schade et al., 1999; van Asperen et al., 2015). In our study, the net CO uptake during night-time indicates that there is a microbial sink for atmospheric CO. We expect that this CO consumption also exists during daytime, and it may be increased due to temperature dependency of the consumption (King, 2000; Whalen and Reeburgh, 2001). At our RCG site the estimated daytime CO consumption is overruled by a simultaneous strong CO production. Assuming a temperature dependent CO uptake (Whalen and Reeburgh, 2001), we estimated that the daytime CO uptake (mean of -1.79 nmol m$^{-2}$ s$^{-1}$) is over two times that in the night (mean -0.77 nmol m$^{-2}$ s$^{-1}$). When we took this into account in gross daytime CO emissions, also daytime CO emission was estimated markedly higher compared to the net measured daytime CO emission.

Strong correlations between daytime $F_{CO}$ and $R_{glob}$ (and other radiation components) indicate that the direct or indirect effects of radiation drive the CO emissions. Correlation between $F_{CO}$ and soil heat flux ($G$), and that between $F_{CO}$ and $T_{air}$ indicate that also thermal degradation plays an important role in daytime CO formation. Although we cannot separate between biotic and abiotic CO formation, the negative correlation between daytime $F_{CO}$ and NEE ($r$=-0.469) during early summer (days 146-160), supporting the findings of Wilks (1959), Bruhn et al. (2013) and Fraser et al. (2015) that CO can be emitted not only from dead plant matter but also from living green leaves. A poor correlation between $F_{CO}$ and ecosystem respiration (RESP) throughout the measurement campaign indicates that microbial and plant respiratory activity does not play an important role in the CO formation. On the contrary, the significant negative correlations between $F_{N2O}$ and night-time $F_{CO}$ ($F_{CO_{night}}$) in the spring ($r$=-0.336), mid-summer ($r$=-0.607) and late autumn ($r$=-0.514) indicate that nitrogen cycling microbes (nitrifiers) may be involved in CO consumption at the RCG site.

CONCLUSIONS

This is the first study to apply EC based techniques to measure seasonal and diurnal variation in $F_{CO}$ at any ecosystem type in the world. We demonstrate that the EC technique provides a useful tool to identify driving variables and processes of $F_{CO}$ at ecosystem level, findings that have previously been shown with plot scale chamber measurements or in the laboratory. At the RCG site, the daytime CO emissions and night-time CO uptake demonstrate the parallel consumption and production processes. Based on daytime and night-time separation of $F_{CO}$, and correlation analysis between $F_{CO}$ and radiation, $T_{soil}$, $T_{air}$, heat fluxes (H, LE), NEE, ecosystem respiration, and $F_{N2O}$, the daytime CO emissions were suggested to be driven mainly by direct and indirect effects of radiation, while the night-time CO uptake was found to be connected to $N_2O$ emissions. In order to fully understand the source-sink dynamics and processes of CO exchange, continuous and long-term $F_{CO}$ measurements in combination with process-based studies are urgently needed.
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SEASONAL CHANGES IN LEAF FLUORESCENCE SPECTRA: CONTROLS AND IMPLICATIONS

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Keywords: SOLAR-INDUCED CHLOROPHYLL FLUORESCENCE, REMOTE SENSING, PHOTOSYNTHESIS.

INTRODUCTION

Chlorophyll fluorescence (ChlF) conveys information on the photosynthetic performance of leaves, plants and vegetation. ChlF are photons of red and far-red light (650-800nm) that are emitted by chlorophyll-a molecules in the photosystems of plants nanoseconds after light quanta have been absorbed. Since ChlF competes for absorbed excitation energy with photosynthesis, its dynamics provide quasi-instantaneous information on the photosynthetic capacity of leaves. Traditional ChlF methods and analysis have been based on active measurements of leaves where ChlF is estimated over a broad range of wavelengths, typically expanding several tenths of nanometres depending on instrument characteristics (Porcar-Castell et al. 2014). Recently, ChlF methods are being rapidly adopted by the remote sensing community to infer the dynamics of vegetation photosynthesis at the ecosystem, landscape and regional scales (Frankenberg et al. 2011; Guanter et al. 2014; Zarco-Tejada et al. 2016). These pioneering studies indicate that ChlF has indeed a high potential to track photosynthetic capacity of vegetation, with applications in precision agriculture, land use management or climate change biology.

Importantly, the methods used in remote sensing applications are substantially different from traditional ones. ChlF (addressed as solar-induced fluorescence, or SIF, when measured from remote sensing platforms) is retrieved within narrow solar or atmospheric absorption bands that can be narrower than 1nm, like the atmospheric O\textsubscript{2}-B and O\textsubscript{2}-A absorption bands, around 687nm and 760nm, respectively, or the Fraunhofer K\textsubscript{I} band around 770nm (Joiner et al., 2011). The fact that SIF can be retrieved only within narrow spectral windows has important implications for data interpretation because the dynamics (and the processes that control them) depend on wavelength (Porcar-Castell et al. 2014). For example, while far-red ChlF bands are not affected by chlorophyll reabsorption, red ChlF can be strongly reabsorbed within the leaf or within a plant canopy so that red and far-red ChlF will be differently affected by changes in leaf or canopy chlorophyll content. Similarly, the spectral properties of the ChlF emission of photosystem II and photosystem I units are different. Accordingly, seasonal changes in the ratio of these two types of photosystems will also affect the spectral dynamics of the ChlF signal.

The question remains to what extent the fluorescence spectra varies over the season, what are the factors that control it, and how do they impact on the SIF as retrieved at different wavelengths. In this study we measured the fluorescence spectra of Scots pine needles during the spring recovery of photosynthesis, together with leaf pigment contents and leaf absorption. Our underlying hypothesis is that SIF is able to track the reactivation of the photosynthetic apparatus during the winter-to-spring transition independently.
of wavelength. However seasonal adjustments in the shape of the fluorescence spectra add wavelength-dependent noise to the relationship.

METHODS

We measured the fluorescence spectra of needles using a white LED light (Magicshine, MJ-858, UK), a FluoWat leaf clip (Image Processing Laboratory, University of Valencia, Spain), a low pass 650nm filter (Edmund Optics Ltd, UK) and an ASD spectrometer (FieldSpec, ASD-Panalytical, Boulder, CO). Needles from the top of five different Scots pine trees growing at SMEAR-II station were regularly sampled. A part of the samples was immediately frozen in liquid nitrogen for subsequent pigment extractions and the other subset was used for optical measurements. Prior to fluorescence spectral measurements, needles were dark acclimated for 1 hour. Light induction kinetics were recorded with the setup described above for 3 minutes until the fluorescence spectra reached a steady state. The fluorescence dynamics at 690nm and 740nm in response to the induction were used to derive the contribution of photosystem I to the total fluorescence signal (Genty et al. 1990). These data was used to assess the impact of PSI fluorescence on the seasonal changes in leaf fluorescence spectra.

In addition, we conducted regular leaf absorption measurements using recently developed method (Olascoaga et al. 2016) and pigment analysis to assess the impact of pigment contents and reabsorption on the seasonal changes in leaf fluorescence spectra.

PRELIMINARY RESULTS

We observed seasonal changes in the shape of the fluorescence spectra of needles during the spring recovery of photosynthesis (Figure 1). These changes could be attributed to the relative contribution of PSI fluorescence in the total signal (Figure 2) as well as to changes in total PAR absorption and structural organization of the photosystems (not shown). The impact and role of these processes is being assessed.

CONCLUSIONS

We here demonstrate that the shape of the fluorescence spectra does not remain constant during the spring recovery of photosynthesis likely due to changes in the spectral contribution of the two photosystems and changes in fluorescence reabsorption. However, the small differences in spectral properties at the O₂-A and O₂-B bands (687 and 760nm) preliminarily suggest that the impact of these processes on the interpretation of remotely sensed data will be small.

Figure 1. Differences in the shape of the fluorescence spectra of Scots pine needles before (open circles) and after (closed circles) the spring recovery of photosynthesis. Spectral data was smoothed using a
Savitzky-Golay filter (order 3, m=5 (spectrometer acquisitions), and m=13 (spectral bands)). The data demonstrates that the spectra is not constant and undergoes changes in the range 680-740nm.

Figure 2. Seasonal changes in photosystem I (PSI) fluorescence contribution to total steady state fluorescence in Scots pine needles. Thick line denotes the average of 5 independent biological replicates (dashed lines). Open points correspond to occasional measurements in the lower canopy (n=5). Error bars are Standard Errors. The data demonstrates that PSI contribution is highly dynamic.

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INTRODUCTION

The total reactivity of hydroxyl radical (OH) is an important tool to assess the exhaustiveness of measurements of individual compounds during intensive measurement campaigns and while monitoring air chemical composition at atmospheric stations. This approach was initiated in the early 2000s (Kovacs and Brune, 2001), based on laser induced fluorescence (LIF) techniques. Shortly thereafter, a more affordable indirect method to measure OH reactivity has been developed, namely the Comparative Reactivity Method (CRM, Sinha et al., 2008). It relies on competition reactions for OH between a reference compound with known reaction rate added to ambient air and do not make use of lasers.

Our group started recently to develop a CRM system that has been carefully characterised through laboratory experiments and modelling. In order to test its performances, the system has been deployed from late January to the end of February 2016 close to the main SMEAR III site (third Station for Measuring Ecosystem-Atmosphere Relations), a semi-urban station in Helsinki, Finland. The results show that the instrument could run for a long period of time and provide insight into winter OH reactivity from this semi-urban site, covering various meteorological conditions with ambient temperatures ranging from -7 to 4°C.

METHODS

The CRM instrument scheme is depicted in Figure 1. Pyrrole (C₅H₅N) is introduced to the system and is monitored by a gas chromatograph with a time resolution of 2-minutes. The system alternate every 8 minutes between measurement of zero air and ambient air. The operating principles are described in Sinha et al. (2008) and are briefly mentioned here. Zero air is assumed to contain only the added pyrrole as reactive gas, so that all OH produced by the photolysis of water (H₂O) is consumed by pyrrole (C₂). Ambient air contains other reactive compounds that compete for OH leading to a higher pyrrole level (C₃). Finally the level of pyrrole in the absence of OH (C₁) is measured by introducing a large concentration of 0.6% propane in N₂ to act as an OH scavenger (Zannoni et al., 2015). The total OH reactivity $R_{eqn}$ is then derived from the following equation:

$$ R_{eqn} = \frac{C_3 - C_2}{C_1 - C_3} k_p C_1 $$

with $k_p$ the reaction rate coefficient of the reaction between pyrrole and OH (1.2·10⁻¹⁰ cm³s⁻¹). C₃ should be corrected for the difference in relative humidity (RH) with C₂ to take into account the variation of OH concentration due to the change of humidity. Also model-based correction factor $F$ is necessary to correct for the first-order kinetics assumption ([C₅H₅N] ≫ [OH]), which is not met during measurements (C₅H₅N/OH ratio varies between 1.5 and 2.2).

$$ R_{true} = R_{eqn} F $$

Additional correction factors due to the presence of nitrogen oxide (NO) and nitrogen dioxide (NO₂) need to be applied (Michoud et al., 2015). NO reacts with peroxy radical HO₂ to produce additional OH, while NO₂ seems to be converted to NO in the CRM system, also leading to an increase in OH levels (and a
lower C$_3$). Finally, ozone (O$_3$) has been found to also increase the amount of OH in the reactor, which also needs to be taken into account.

![Figure 1.](image)

Figure 1. Comparative Reactivity Method instrument scheme. (MFC: Mass Flow Controller; GC: Gas Chromatograph; UV: ultraviolet; N$_2$: nitrogen; H$_2$O: water)

In addition to total OH reactivity measurements reactive organic compounds were also measured with an in situ GC-MS (C$_6$-C$_{10}$ hydrocarbons) and sampled 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 $R$ 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.

$$ R = \sum_i k_{OH+X_i} [X_i] $$

(3)

Our analysis includes 57 individual species from GC-MS, GC-FID and LC-UV measurements. In addition, nitrogen oxides were monitored by an APNA-370 NO$_x$ monitor and ozone, sulfur dioxide, and carbon oxide were retrieved from the mast of the SMEAR III station, about 85 m away from our measurement container.

RESULTS AND DISCUSSION

The hourly averaged reactivity measured between 29 January and 24 February was 23.3 ± 6.1 (1σ) s$^{-1}$. No clear diurnal pattern was found. This magnitude is similar to other winter studies in urban environments (e.g. Kovacs et al., 2003; Ren et al., 2006; Yoshino et al., 2012). However, difference between calculated and measured OH reactivity was much larger in our study (up to 90%). The difference can be partly explained by the absence of specific reactive compounds from our ancillary measurements. It is also
possible that due to a situation with lower temperatures, higher NOx levels, and short days could contribute to the formation of organonitrate compounds that have not been taken into account in this study. This class of compounds might be responsible for another fraction of the unexplained reactivity.

Reactivity peaks due to NO emissions from trucks and vehicles next to the measurement container were registered by our system, but the measured values (not shown) on these occurrences were much higher than the calculated values, which is likely due to co-emitted compounds that were not measured. Possibly carbon oxide that was not measured directly at our container was also emitted by trucks and could contribute to the high values of reactivity measured.

CONCLUSIONS

The CRM system developed at FMI was tested during winter months at the SMEAR III station in Helsinki. It performed well for a while month of measurements, with total OH reactivity values close to values measured in other urban environments in the winter. No clear pattern could be observed for the reactivity, but high peaks corresponding to nearby delivery vehicles were captured. However, the calculated OH reactivity based on 62 individual compounds was found to be much lower than the total measured OH reactivity. This might be due to compounds (e.g. organonitrates) that were not considered in this study.

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EDDY COVARIANCE INSTRUMENT COMPARISON

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Keywords: EDDY COVARIANCE, CO₂ 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 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 (CO₂ 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, not the fast-response one (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 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, CO₂ and H₂O 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 CO₂ sensors CARBOCAP GMP343, Vaisala Oyj, Vantaa, Finland;
- logging:
  Windows computer.

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The instruments are visible in Figure 1.

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

The results are currently under evaluation. Specifically, the difference of the two recorded CO$_2$ fluxes ($F_{CO2}$) is being analysed. Particular attention to the relationship between the difference of the fluxes ($\Delta F_{CO2}$) and the sensible heat flux (SH) is being paid, given that it has been hypothesised that the Irgason might have a temperature-driven bias. Moreover, the relationship of $\Delta F_{CO2}$ with any other relevant variable will also be investigated.

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137Cs DISTRIBUTIONS IN SOIL AND TREES IN FOREST ECOSYSTEMS AFTER THE RADIOACTIVE FALLOUT – COMPARISON STUDY BETWEEN SOUTHERN FINLAND AND FUKUSHIMA, JAPAN

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Keywords: CHERNOBYL, CONIFEROUS FOREST, SOIL, FUKUSHIMA DAIICHI NUCLEAR POWER PLANT, RADIOCESIUM.

INTRODUCTION

Two serious nuclear accidents, Fukushima in 2011 and Chernobyl in 1986 resulted in strong radioactive fallouts in Japan and in Eastern and Northern Europe. After the accidents, large areas were highly contaminated by radioactive nuclides, especially by iodine (131I and 133I) and cesium (134Cs and 137Cs). The areas of Fukushima and Southern Finland are somewhat similar regarding land use and forested area. The similarities between the forested areas of Fukushima and S. Finland create an ideal comparison to explore the dynamics and impact of 137Cs contamination in forest ecosystems. The two nuclear accidents provide a unique possibility to compare the distribution pattern and decay of 137Cs in forest ecosystems in the short- and long-term. The changes taken place in Southern Finland over the last 25 years after the Chernobyl accident also provide valuable information for predicting the distribution pattern of 137Cs in trees, ground vegetation and soil in the forests of Fukushima area in the coming years. The overall aim of this study was to determine 137Cs distribution in forests shortly after the radioactive fallout and estimate their long-term changes by comparing 137Cs activities in different parts of forests in Southern Finland and Fukushima areas.

METHODS

The study site, Hyytiälä in Southern Finland is located at the Station for Measuring Ecosystem-Atmosphere Relationships, SMEARII (61°51′ N, 24°17′ E, 180m asl). The external exposure rate of this region in April 1986 was 0.5 mR h⁻¹ (around 4.5 µSv h⁻¹) (Hari et al., unpublished data). The site was sown with P. sylvestris on burned, mechanically prepared soil in 1962. The average stand height at the site was 12.6 m in 1995 with an average diameter of 0.16 m. In 2013, the respective values were 18.6 m and 0.18 m (Ilvesniemi et al., 2009). In the Fukushima area, the study was conducted in the upper part of
Kami-Oguni River catchment in Ryozencho, Date ville in Fukushima prefecture (37° 43´ N, 140° 34´ E, 370m asl). It locates about 50 km northwest of Fukushima Nuclear Power Plant. The catchment size is 18.9 ha. According to the radioactivity survey report, which used aircraft survey devices, the air dose rate of this region and total deposition rate of $^{137}$Cs in December 2012 was 1.9-3.8 µSv h$^{-1}$ and 300-600 kBq m$^{-2}$, respectively (Ministry of Education, Culture, Sports, Science and Technology Japan, 2012). The study site consisted of a cedar stand (*Cryptomeria japonica*) with an average height of 22.5 m, an average diameter of 0.269 m and the tree density of 2000 trees ha$^{-1}$. Geological settings of the catchment are dominated by volcanic rocks (andesite and basalt) formed by volcanic eruptions during the Miocene epoch.

We measured the radioactivity originating from $^{137}$Cs from samples collected from different parts of both forest ecosystems (needles, stem and from different depths of soil) by Ge semiconductor detector (GMX15P4-70, Seiko EG&G, Tokyo, Japan) and soil samples collected in 1995 and 2013 by a well-type NaI(Tl) scintillation counter (ARC-300, Aloka, Tokyo, Japan). For studying the long-term pattern in the distribution of the radioactive fallout the samples collected from Hyytiälä in 1986, 1995 and 2013 were analysed. In Fukushima, the samples were collected in 2012 and 2014, 2-3 years after the accident.

**RESULTS**

The highest $^{137}$Cs concentrations were observed in the uppermost surface layers of the soil, and they decreased exponentially deeper in the soil. We also observed that $^{137}$Cs activity concentrations estimated from the samples in 1995 and 2013 in Finland showed different behaviour in the surface soil layers compared to the deep soil layer. The $^{137}$Cs activity concentrations in the needle litter collected from the litter traps were almost equal in the samples collected in 1995 and 2013 (Fig. 1). However, in soil samples, there was a large difference between the samples collected in 1995 and 2013 in the topsoil as well as in the 10-20 cm. Our results suggested that the $^{137}$Cs nuclei were still mobile in the surface soil layers 27 years after the accident. Despite its mobility and active role in the metabolism of trees, the $^{137}$Cs remains in the structure of the trees for decades, and there is not much exchange of $^{137}$Cs between the heartwood and surface layers of the stem. Since the $^{137}$Cs belongs to the same group of elements as potassium, $^{137}$Cs is taken up by plants aside with potassium although $^{137}$Cs is not used as a plant nutrient. The $^{137}$Cs remains in the internal cycle of the forest ecosystem for decades, which also is reflected in the $^{137}$Cs activity concentrations in the surface layers of the soil through litter input.

**ACKNOWLEDGEMENTS**

This study was supported by a grant (24248027) for scientific research from the Ministry of Education, Culture, Sports, Science and Technology Japan Society for the Promotion of Science. We also thank for the Academy of Finland Finnish Centre of Excellence program (grant no 72041) for financing the study in Finland. This work was supported by the National Council for Aerosol Research under grant A1/001.

**REFERENCES**


MODELING STUDY ON EXTREMELY LOW-VOLATILITY ORGANIC COMPOUNDS (ELVOCS) AND NEW PARTICLE FORMATION (NPF) AT SMEAR II STATION IN BOREAL FOREST OF FINLAND AND SORPES STATION IN URBAN AREA OF CHINA

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Key words: MALTE-BOX MODEL, ELVOCS, NPF, PARTICLE COMPOSITION.

INTRODUCTION

New particle formation (NPF), as a significant source of aerosols, was observed all over the world. Recently, extremely low volatility compounds (ELVOCs) become a hot topic because of their contributions to the nucleation and subsequent growth. Monoterpene oxidation by ozone was found to be a main source of ELVOCs. Based on the theory presented by Ehn et al. 2014, a ELVOCs chemistry module was developed. This ELVOCs chemistry module, combined with MALTE-BOX model was used to simulate the ELVOCs concentrations and NPF both at boreal forest site (i.e. SMEAR II) in Finland and urban site (i.e. SORPES) in China. The differences of submicron particle compositions during NPF at two sites were investigated.

METHODS

This study used MALTE-BOX model, a zero-dimensional model, which includes several modules for the simulation of chemical and aerosol dynamical processes (Boy et al., 2006). The gas-phase chemistry was simulated using the Master Chemical Mechanism version 3.3 (MCMv3.3), which is a near-explicit oxidation scheme. The ELVOCs chemistry module, which is constructed based on the theory presented by Ehn et al. 2014, was added into the MCMv3.3. The aerosol dynamical processes were simulated with the size-segregated aerosol model, UHMA (University of Helsinki Multicomponent Aerosol model). The measurement variables, i.e. meteorological conditions (Temperature, Relatively Humidity, Pressure,
Radiation), trace gases concentration (SO$_2$, O$_3$, NO, NO$_2$, CO) and VOCs (Methane, Propane, ethylene, ethane, Methanol, Acetaldehyde, Acetone, Acetic acid, Isoprene, Benzene, n-Butane, MVK, α-pinene, β-pinene, Limonene, Carene), were input into the MALTE-BOX model every 10 min. As no monoterpene measurement at SORPES was available, monoterpene concentration at SORPES was simulated by WRF-chem. The measured aerosol number size distribution was read into the model during the first five hours. The vapor pressures of ELVOCs are calculated using SIMPOL. Boundary layer dilution was also considered in MALTE-BOX. Five case days at SMEAR II, including four NPF event days (1$^{st}$ of May, 2013; 16$^{th}$ of May, 2013; 22$^{nd}$ of May, 2013; 15$^{th}$ of June, 2013) and one non-event day (23$^{rd}$ of April, 2013), were chosen to study. In addition, one NPF event day (4$^{th}$ of October, 2014) at SORPES was simulated.

RESULTS AND CONCLUSIONS

As shown in Fig. 1, the model worked well in simulating ELVOC monomers, ELVOC nitrates and ELVOC peroxy radicals but overestimated the ELVOC dimers. For the ELVOC monomers, the simulated concentration is elevated at daytime, which was similar to the measurement. But the model failed to capture the second peak at 20:00 LT. One possible explanation to this second peak could be formation of ELVOC monomers induced by reactions between monoterpenes and the NO$_3$ radical. The simulated diurnal pattern of ELVOC nitrates was similar with the measurement. Considering a factor of 3 in the uncertainty of the measurements, the simulated results of ELVOC nitrates were acceptable. For the ELVOC peroxy radicals, the simulated diurnal variation differed compared to the measurements but the concentrations of simulated and observed ELVOC radicals were similar. Although the simulated ELVOC dimers had similar diurnal pattern as the measurements, the model overestimated the ELVOC dimers about one order of magnitude.

![Figure 1. Average modeled and measured diurnal circles of (a) ELVOC monomers, (b) ELVOC dimers, (c) ELVOC nitrates, (d) ELVOC radicals.](image-url)
ELVOC dimers, (c) ELVOC nitrates and (d) ELVOC peroxy radicals at SMEAR II in Finland. Note: Measurement average (line) and ±1 standard deviation (shaded area) are in blue; model average (line) and ±1 standard deviation (shaded area) are in red.

The simulations were also conducted for the new particle formation at the urban SORPES station in China. Figure 2 presents the observed and simulated particle number size distributions and the composition of sub-100 nm particles at both stations. Only monoterpenes were considered to form ELVOC in the model. To capture the new particle formation at SORPES, the input concentration of monoterpane (simulated by WRF-chem) had to be multiplied by a factor of 3. It means that at this urban site more ELVOCs or LVOCs need to form from oxidation of other anthropogenic VOCs, in order for the model to capture the observed particle growth. The codes about ELVOCs formation from the oxidation of aromatic compounds are being worked on. With this scaling factor, the model can capture the shapes of new particle formation at SORPES. Because of much higher SO\textsubscript{2} concentrations in the urban areas of China, the H\textsubscript{2}SO\textsubscript{4} contributed strong to the growth of newly formed particles. ELVOC nitrate gave more contributions to the growth at SORPES than at SMEAR II. It is mainly because high NO concentration at SORPES suppresses the production of ELVOC dimmers but promotes the formation of ELVOC nitrates. More researches, especially ELVOCs measurements, are needed at urban sites like SORPES.

![Figure 2](image)

Figure 2. Observed number size distribution (upper panels), simulated number size distribution (middle panels) and simulated compositions of sub-100 nm particles (lower panels) at (a) SMEAR II on 15\textsuperscript{th} of June, 2013 and (b) SORPES on 4\textsuperscript{th} of October, 2014.

ACKNOWLEDGEMENTS
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REFERENCES

IMPACT OF TEMPERATURE ON THE FORMATION OF HIGHLY OXIDIZED MOLECULES (HOMS)

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Keywords: HOMS, MASS SPECTROMETRY, CI-API-TOF.

INTRODUCTION

The existence of highly oxidized multifunctional molecules (HOMs) in the atmosphere was recently shown (Ehn et al., 2012; 2014) as a resulting product from the oxidation of biogenic vapors released by terrestrial vegetation. Such species are believed to significantly contribute to the formation of Secondary Organic Aerosol (SOA) influencing Cloud Condensation Nuclei (CCN) formation processes and thereby climate. Our recent work (Quéléver, 2015) has shown that a change of temperature may impact the behavior of HOMs formed upon oxidation of α-pinene. Thus, our continuing task was focused toward quantifying HOM formation as a function of temperature within an atmospherically-relevant range. The hypothesis of this work was that the autoxidation known to produce the HOM (Ehn et al, 2014), specifically the hydrogen atom abstractions, should become easier as temperature increases. Thereby we expect higher oxidation levels at higher temperatures.

METHODS

A new flow tube setup was designed and constructed in order to allow a temperature range from 0 to 50°C. The system is composed of a quartz flow tube enclosed in an aluminium block (Figure 1). A system of copper tubing inserted inside the main block and connected to an external thermo-regulated bath (thermostat) enables to obtain a homogeneous temperature inside the flow tube. The final assembly was tested to be suitable for cooling down to 0°C and warming up to 50°C inside the flow tube while using a mixture of ethylene glycol - water (1:1) as liquid bath. The 1m-long flow tube, with an inner diameter of 50mm, was thermally controlled over 90% of its surface. An adjustable injector for the α-pinene was placed at 1/3 of the flow tube giving a residence time of about 6s inside the heated/cooled region of the setup.

Figure 1. Scheme of the experimental setup
The oxidized molecules produced by the reaction between α-pinene and ozone were measured with a nitrate-based chemical ionization atmospheric pressure interface time of flight (CI-APi-TOF; Jokinen et al. 2012) mass spectrometer. The evolution of the signal for specific compounds of known chemical composition was followed as a function of temperature (Figure 2). As illustrated by the figure bellow, the increase of temperature results in further autoxidation stages, implying more oxidized molecules even within a temperature range typical for the atmosphere.

![Figure 2. Temperature series of HOMs detected as adduct with nitrates (NO$_3^-$). The selected molecules are representative of 3 generations of oxidation where only the number of oxygen molecules added to parent structure is changing (each species are separated by 32 Da).](image-url)

CONCLUSIONS

Our work explicitly shows that temperature impacts the autoxidation mechanism involved in the formation of HOMs derived from monoterpenes. Even relatively small increases in temperature can cause a significant increase in the average level of oxidation of the HOMs. This, in turn, may have consequences for the ability of the HOMs to take part in the formation and growth of new particles. These results will be compared to ambient observations of HOMs in the boreal forest.

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REFERENCES


HIMMELI – Helsinki Model of MEthane build-up and emIssion for peatlands

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Keywords: peatland, modelling, methane, plant transport, ebullition.

INTRODUCTION

In order to predict the future atmospheric greenhouse gas concentrations it is essential to know the dynamics of wetland methane (CH₄) emissions. Studying them by using the modelling approach has been active in recent years (Melton et al., 2013, Wania et al., 2013, Xu et al., 2016). So far, most of the advanced process-based wetland models represent northern peat-forming wetlands, and the standard ecosystem type is a treeless peatland that has gas-transporting herbaceous vegetation.

Peatlands emit CH₄ because oxygen (O₂) concentrations in their water-saturated soils are low. Anoxic decomposition of soil organic matter is partly carried out by methanogenic microbes that produce CH₄ (Nilsson and Öquist, 2009). Anoxia has also forced vascular peatland plants to develop techniques to get O₂ to their roots that extend to the inundated soil layers. For example, sedge species from genera Carex and Eriophorum have aerenchyma, special tissue with air-filled spaces that allows diffusion of O₂ from the atmosphere to the roots (Moog and Brüggemann, 1998). As a by-product, this tissue also facilitates transport of CH₄ to the atmosphere (Morrissey et al., 1993). In addition to transfer via plants, CH₄ is known to be emitted from peatlands as ebullition, i.e. release of CH₄ bubbles into the atmosphere, and by diffusion through the peat column. Methanotrophic bacteria derive their energy by oxidizing CH₄ to CO₂. Rate of the CH₄ oxidation reaction depends on the concentrations of both CH₄ and O₂ and since CH₄ oxidation is a biochemical reaction, the rate also is limited by factors that affect the microbial activity, such as temperature (Whalen and Reeburgh, 1996). All the three transport mechanisms and the CH₄ oxidation have been implemented in many peatland models in which the peat column is divided into several layers and physically-based formulations simulate the carbon processes in them.

We have built up a model that takes as input the rate of anoxic peat respiration and computes the subsequent CH₄ emissions of a peatland by simulating the transport of CH₄, O₂ and CO₂ and the oxidation rate that depends on the prevailing O₂ concentration. We largely adopted the process descriptions from earlier models (e.g. Wania et al., 2010). The aim was to obtain a robust and flexible module that can be used as a submodel within different soil carbon models. In this paper, we present the model and results from standalone tests whose purpose was to study the general behavior of the model, quantify how sensitive the model outputs are to the input, and understand how this depends on the model dynamics.
MODEL DESCRIPTION

The model HIMMELI (HelsInki Model of MEthane buILd-up and emIssion) (Fig. 1) is driven with peat temperature, leaf area index (LAI) of aerenchymatous gas-transporting vegetation and water table depth (WTD), and it needs as input the carbon (C) input rate, i.e., the rate of anoxic respiration per 1 m² of the peatland. The anoxic respiration rate needs to be simulated with another model (e.g., Schuldt et al., 2013). 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 as well as the fraction of oxidized CH₄. The current set-up of the model runs in 1-day resolution, taking the input as daily averages. The differential equations are solved using the fourth order Runge-Kutta method.

Figure 1. A schematic description of the model HIMMELI. An essential role is played by the root distribution that determines the CH₄ production rate and plant transport capacity at different depths.

MODEL TESTING

We tested the model by running it into equilibrium with several different input value combinations. Specifically, we tested the sensitivity of the model outputs to rate of anoxic respiration, peat temperature, WTD and LAI (and corresponding root mass), by varying these one by one. The values varied within realistic limits. In these experiments, the anoxic respiration rate was always allocated only in the inundated peat layers. Temperature was always constant across all the soil profile.

PRELIMINARY RESULTS AND DISCUSSION

Input anoxic respiration rate and the subsequent CH₄ production potential had a significant impact on the resulting CH₄ emissions. The final total emissions depended strongly on the maximum potential production and were only modified by the LAI and WTD. The dependency was linear with R² of 1.0 in the cases that LAI was zero and around 0.99-1.0 in the cases with LAI of 1 m² m⁻². The percentage of maximum potential CH₄ production released as CH₄ emission varied between 21% and (almost) 100%, the smallest percentages occurring with the lowest anoxic respiration rates and, on the other hand, generally the lowest values came from the experiment with LAI was 1 and WTD was 0 (exactly at the peat surface). The highest emissions were released when both WTD and LAI were zero.
The different transport routes naturally followed the strict division that when LAI was 0, there was no plant transport, and with WTD below the peat surface, direct ebullition fluxes into the atmosphere were zero since the gas bubbles continued via diffusion in the air-filled peat after being released from the water. Increasing LAI increased the contribution of plant transport in the total CH$_4$ emission, however, the higher the respiration rate, the smaller percentage of produced CH$_4$ was released via plants. The mechanism probably was that the higher CH$_4$ production rate resulted in higher CH$_4$ concentrations that were readily released into the atmosphere as ebullition.

Our results showed the importance of O$_2$ that inhibits CH$_4$ production and enables oxidation of CH$_4$ to CO$_2$ in the peat. In general, the more O$_2$ was transported to the soil layers that produced CH$_4$, the less CH$_4$ was produced and later emitted. As a conclusion, although increasing LAI increases the CH$_4$ plant transport capacity that intuitively could mean higher CH$_4$ emissions, the impact of increasing also plant transport of O$_2$ into the soil was so strong that as a result, total CH$_4$ emissions decreased. It should be remembered, though, that the CH$_4$ production, or anoxic respiration rate, was not dependent on LAI in our experiments. This probably is not true in the nature where the root exudates of gas-transporting plants have been suggested to be a significant source of CH$_4$ substrates (Whiting and Chanton, 1993), and hence a greater LAI would also mean higher substrate input. Impact of temperature on the CH$_4$ emissions was also transmitted via O$_2$ availability. The total CH$_4$ emissions increased slightly with temperature. The main reason for this obviously was that in cold temperatures, the solubility of gases and thus the concentrations of dissolved O$_2$ in water were higher, therefore, the CH$_4$ oxidation and inhibition of CH$_4$ production were highest in low temperatures although the reaction rates were lower.

ACKNOWLEDGEMENTS

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REFERENCES


CLIMATE CHANGE INDUCED pH DECREASE IN THE SENSITIVE LAKE ECOSYSTEMS – “OCEAN ACIDIFICATION” IN LAKES

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Keywords: LAKE ACIDIFICATION, CARBON DIOXIDE, CLIMATE CHANGE

INTRODUCTION

The release of carbon dioxide (CO₂) from anthropogenic sources since the beginning of the industrial era has resulted in an increase in atmospheric CO₂. Oceans have absorbed about 30% of these emissions slowing down the increase of atmospheric concentration of CO₂ (Sabine et al. 2004). However, when CO₂ is absorbed by seawater, dissolved CO₂ induces chemical reactions that reduce both seawater pH (i.e. increase H⁺ concentration) and the concentration of carbonate ions. This whole process is called ocean acidification. Ocean acidification has been shown to seriously affect calcifying organisms like corals and coccolithophores such as the bloom forming *Emiliania huxleyi*. By affecting the base of the food webs, ocean acidification has also serious consequences to global carbon cycling. In the end of the previous century acidifying sulfur and nitrogen deposition seriously affected both terrestrial and freshwater ecosystems, but intensive reduction of atmospheric emissions in 80s and 90s lead to recovery of the acidified soils and waters. Globally, most sensitive to the anthropogenic acidification are areas situated on the Precambrian bedrock providing little base cations to buffer acidification. So far, no reports of the effects of increasing atmospheric CO₂ on pH of lakes have been published. Lakes may respond differently from open oceans to acidification due to their lower alkalinity and buffering capacity, and also a greater natural variability in pH and related parameters.

The hypotheses of this study are: 1) The pH in boreal lakes will gradually and slowly decrease as the atmospheric CO₂ level increases due to anthropogenic CO₂ emissions. 2) The recovery of the lakes from acidification caused by high anthropogenic sulphur and nitrogen deposition has masked the effects of changing CO₂ levels on pH 3) Because carbonic acid (H₂CO₃) is a weak acid, increasing atmospheric CO₂ will lower pH in lakes but not markedly decrease alkalinity.

METHODS

We utilized the data from ‘The Regional Monitoring of Lake Acidification (RMLA) – network that was established in 1980s and 1990s to monitor the acid sensitive lakes in Finland (Mannio and Vuorenmaa 1995). RLMA lakes cover the whole country with focus on small, poorly buffered seepage and headwater lakes. They are sampled in autumn, mainly in October or November, or both. The study period was chosen to be the latest 15 years prior to present, i.e. 2000-2015, because during this period the acid deposition was already markedly cut down and the most drastic changes in lake pH due to recovery from acidification had already taken place (Vuorenmaa and Forsius 2007). As a reference, we also studied the 15 year period prior the actual study period i.e. 1984-1999. We used Mann-Kendall test (Hirsch et al., 1982, 1991) to identify the trends in lake water pH during the study period.
RESULTS

As hypothesized, all of the studied RLMA lakes showed recovery from previous anthropogenic acidification indicated by increasing pH in 1984-1999 (Table 1). Also supporting our hypothesis, by 2015 in 9 lakes increasing trend in pH had turned into a decreasing trend, and furthermore, in 3 lakes an increasing trend in pH had levelled showing no significant trend between 2000 and 2015 (Table 1). In most of the lakes alkalinity showed an increasing trend between 2000 and 2015 (Table 1) as hypothesized.

Table 1. Trend of pH in 1985-1999 and trends in pH and alkalinity 2000-2015. The lakes are arranged according to latitudinal location from South to North. ND no data.

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CONCLUSION

Increasing atmospheric CO₂ will decrease pH in the most sensitive lakes on Precambrian bedrock.

ACKNOWLEDGEMENT

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REFERENCES


**OZO: a software for solving a generalized omega equation and the Zwack-Okossi height tendency equation using WRF model output**

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Keywords: omega equation, height tendency, WRF model

**INTRODUCTION**

Today, high-resolution atmospheric reanalyses provide a three-dimensional view on the evolution of synoptic-scale weather systems (Dee et al., 2011). On the other hand, simulations by atmospheric models allow exploring the sensitivity of both real-world and idealized weather systems to different factors, like the initial state or boundary conditions. Nevertheless, the complexity of atmospheric dynamics often makes the physical interpretation of reanalysis data and model output far from simple. Therefore, there is also a need for diagnostic methods that help to separate the effects of individual dynamical and physical processes on the structure and evolution of weather systems.

Two variables that are of special interest in the study of synoptic-scale weather systems are the geopotential height tendency and vertical motion. Height tendencies are directly related to the movement and intensification or decay of low and high pressure systems. Vertical motions affect atmospheric humidity, cloudiness and precipitation. They also play a crucial role in atmospheric dynamics by inducing adiabatic temperature changes, by generating cyclonic or anticyclonic vorticity, and by converting available potential energy to kinetic energy (Lorenz, 1955).

Here, we introduce a software package (OZO) that can be used for diagnosing the contributions of different dynamical and physical processes to atmospheric vertical motions and height tendencies. OZO calculates vertical motion from a quasigeostrophic and a generalized omega equation (Räisänen, 1995), while height tendencies are calculated using the Zwack-Okossi tendency equation (Zwack and Okossi, 1986). OZO has been tailored to use output from Weather Forecast and Research (WRF) model (Shamarock et al., 2008) simulations run with idealized Cartesian geometry. Due to the wide use of the WRF model, we expect OZO to be a useful open source tool for both research and education.

**METHODS**

The generalized omega equation is a diagnostic tool for estimating atmospheric vertical motions and studying their physical and dynamical causes. The omega equation used in OZO is identical with the Eq. (1) in Räisänen (1995) (not shown). By solving the equation using homogenous boundary conditions ($\omega = 0$ at the bottom and top of the atmosphere), the vertical motion field can be described as a sum of its components:

$$\omega = \omega_V + \omega_T + \omega_F + \omega_Q + \omega_A$$  \hspace{1cm} (1)

where the five $\omega$-terms ($i = V, T, F, Q, A$) represent the contributions from different physical or dynamical processes. $\omega_V$ is the vertical motion associated with vorticity advection, $\omega_T$ thermal
advection, $\omega_F$ friction, $\omega_Q$ diabatic heating and $\omega_A$ is associated with an imbalance between vorticity and temperature tendencies.

Geopotential height tendencies are calculated from the geostrophic vorticity tendency by the equation:

$$\frac{\partial Z}{\partial t} = \frac{f}{g} \nabla^2 \frac{\partial \zeta_g}{\partial t}$$

(2)

The geostrophic vorticity tendency at level $p_L$ is obtained from the Zwack-Okossi tendency equation (Zwack and Okossi, 1986; Lupo and Smith, 1998):

$$\frac{\partial \zeta_g}{\partial t} = \frac{1}{p_s - p_t} \int_{p_s}^{p_t} \left( -V \cdot \nabla (\zeta + f) - \omega \frac{\partial \zeta}{\partial p} + (\zeta + f) \frac{\partial \omega}{\partial p} + k \cdot \left( \frac{\partial V}{\partial p} \times \nabla \omega \right) + k \cdot \nabla \times F \right) dp$$

(3)

After that, analogously with the vertical motion, the height tendency is divided in OZO to the contributions of different physical and dynamical processes as

$$\frac{\partial Z}{\partial t} = \left( \frac{\partial Z}{\partial t} \right)_V + \left( \frac{\partial Z}{\partial t} \right)_T + \left( \frac{\partial Z}{\partial t} \right)_F + \left( \frac{\partial Z}{\partial t} \right)_Q + \left( \frac{\partial Z}{\partial t} \right)_A$$

(4)

Our method differs from earlier applications of the Zwack-Okossi equation (e.g. Lupo and Smith, 1998) because the use of the generalized omega equation eliminates vertical motion as an independent height tendency forcing. This is an important advantage, because these earlier studies have shown a tendency of compensation between vertical motions and the other forcing terms.

The first version of the OZO software package is tailored to use output from WRF simulations in idealized Cartesian geometry. The calculations presented in our study used input data from an idealized moist baroclinic wave simulation, which simulates the evolution of a baroclinic wave within a baroclinically unstable jet in the Northern Hemisphere. The model domain is 4000 x 8000 x 16 km, with 100 km horizontal resolution and periodic boundary conditions in the zonal direction.

OZO can be run on a basic laptop with Linux environment, provided that standard NetCDF library, Intel’s Math Kernel Library and some Fortran compiler, preferably GNU’s gfortran, are available. The source code of the OZO is written in Fortran 90 standard and can be currently compiled only for a serial version.

RESULTS

As a brief illustration of the OZO functionality, results of the height tendency diagnostics are shown. The contributions of the individual height tendency components are in Fig. 1. The values are shown at 900 hPa level, which is sufficiently low to represent the processes affecting the low-level cyclogenesis. Negative (positive) height tendency over the low centre indicates deepening (weakening) of the low.

Vorticity advection (Fig. 1a) produces a wide and strongly positive height tendency behind the surface low. Thermal advection (Fig. 1b) causes a positive height tendency in the area behind the surface low and a negative height tendency at the opposite side. This large negative height tendency ahead of the low is caused by warm air advection in the mid- and upper troposphere. In this baroclinic life cycle simulation, thermal advection is the main contributor to the movement of the cyclone. Friction (Fig. 1c) always acts to damp synoptic-scale weather systems and is thereby
inducing a positive (negative) height tendency over the surface low (high). In contrast to friction, diabatic heating (Fig. 1d) is causing uniformly negative lower tropospheric height tendencies in the vicinity of the surface low. As its contribution is also negative at the centre of the surface low, this indicates that diabatic heating plays an essential role in the deepening the cyclone. The largest negative height tendency due to diabatic heating is located south-east from the low centre, where strong latent heat release occurs in connection with frontal precipitation. The imbalance term (Fig. 1e) shows more small-scale structure than the other terms. In general, however, it is in phase with the total height tendency near the centre of the low, with negative values to the east and positive values to the west.

Figure 1: Height tendencies induced by a) vorticity advection, b) thermal advection, c) friction, d) diabatic heating and e) imbalance term. The sum of all five terms is in f). Values are from the 900 hPa level slightly before the cyclone reaches its maximum intensity. Unit is m/2h and contour lines show 900 hPa geopotential height with 50 m interval.

CONCLUSIONS

The calculated total vertical motions and height tendencies in the test case are generally in excellent agreement with the vertical motions and height tendencies diagnosed directly from the WRF simulations. The time-averaged correlation between the calculated and the WRF height tendency was 0.95-0.98 in the troposphere. For the vertical motion as well, a correlation of 0.97 was found in the midtroposphere. Our analysis further illustrates the importance of both adiabatic and diabatic processes to atmospheric vertical motions and the development of the simulated cyclone.
The OZO software is applicable to different types of WRF simulations, as far as Cartesian geometry is used. One example of potential applications are simulations with increased sea surface temperatures as the lower boundary condition. Combined with OZO, such simulations provide a simple framework for studying the changes in cyclone dynamics in a warmer climate.

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REFERENCES


OXIDATION OF AROMATIC COMPOUNDS AS A SOURCE OF ANTHROPOGENIC HIGHLY-OXIDIZED MULTIFUNCTIONAL COMPOUNDS (HOMs)

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Keywords: Autoxidation, Aromatics, Peroxy radicals, SOA precursors

INTRODUCTION

Gas-phase oxidation of volatile organic compounds (VOCs) is an important source of atmospheric secondary organic aerosol (SOA). Aromatic compounds comprise a large fraction of anthropogenic VOC emissions, and are produced generally by combustion processes and petroleum industry, but nonetheless have also significant natural emissions. Aromatics are a well-known source of SOA especially at urban atmospheres (Ziemann and Atkinson 2012), but the efficiency and the mechanistic routes leading to SOA formation are currently uncertain (Hildebrandt, L. et al. 2009).

Recently, a highly efficient pseudo-one-step gas-phase VOC oxidation process has received considerable attention as a potential pathway to very low-volatile condensable material - which is needed in the first-steps of ambient SOA formation (Riipinen et al. 2011, Ehn et al. 2014). This process is called autoxidation (Crounse et al. 2013, Rissanen et al. 2014) and it requires only a single-oxidant attack, leading to highly-oxidized multifunctional compounds (HOMs) in sub-second time-scales. The process is autocatalytic and after the initiation reaction relies only on the specific molecular structures which facilitate internal isomerization reactions, progressing the pseudo-unimolecular oxidation sequence. The phenomena was first observed with biogenic monoterpenes (i.e., unsaturated C_{10}H_{16} compounds) and endocyclic alkenes (Crounse et al. 2013, Ehn et al. 2014), but preliminary experiments have indicated that highly-oxidized species form also during aromatic oxidation. However, aromatics are exceptionally stable VOCs with a rigid benzene ring as an integral unit and thereby the autoxidation mechanisms generated for simpler cyclic alkenes (Mentel, et al. 2015, Rissanen, et al. 2015) are not directly applicable to the aromatic oxidation system.

Currently the oxidation of aromatics is thought to evolve through bicyclic peroxy radical intermediates as radical chain carriers (e.g., Atkinson 1989, Andino et al. 1996 Birdsell, et al. 2010), and the formation of HOM in the aromatic oxidation likely involves these species. The purpose of the present study was to investigate the detailed mechanistic VOC oxidation steps leading to the highly-oxidized product species, and to illustrate whether these highly-oxidized species can participate in ambient aerosol formation.

METHODS

Flow reactor and environmental chamber investigations were performed to characterize gas-phase HOM formation from photo-oxidation of various aromatic VOCs. Chamber experiments with aerosol seed addition were also performed to determine the potential of these species to act as a source of SOA. All the flow reactor investigations were performed in University of Helsinki with a suite of different surface-to-volume glass flow tube reactors enabling to experiment photochemistry and different experimental
conditions. Environmental chamber experiments were conducted in glass build Jülich Plant Atmosphere Chambers (JPAC in Forschungszentrum Jülich, Germany) and in University of Helsinki dual-Teflon chambers. The combination of flow tube and chamber platforms extends the experimental conditions significantly and allows to investigate, for example, the influence of different residence and gas-wall interaction times, which can be highly beneficial in analysing the results, enabling to separate instrumental dependencies from the experimental data.

In Helsinki flow reactors, oxidation of selected aromatic VOCs (benzene C$_6$H$_6$, toluene C$_7$H$_8$, xylene C$_8$H$_10$, naphthalene C$_{10}$H$_8$ and anthracene C$_{14}$H$_{10}$) were investigated in order to characterize the autocatalytic oxidation pathways. In all of these experiments the detection of reaction products was monitored by a suite of Chemical Ionization Atmospheric Pressure Interface Time-of-flight (CI-APi-TOF) mass spectrometers employing nitrate (NO$_3^-$), iodide (I$^-$) and proton transfer (H$^+$) ionization. This combination of reagent ions enables to detect products with various levels of oxidation. In addition, a suite of other gas-phase analysis methods was applied to monitor the experimental conditions and the evolution of the reacting gas-mixture. In JPAC chambers benzene and deuterated benzene (C$_6$H$_6$ and C$_6$D$_6$), and phenol (C$_6$H$_5$OH) oxidation experiments were performed in order to deduce the highly-oxidized product yields and their contribution to SOA formation. Also in Helsinki chamber, benzene oxidation was further studied to understand the oxidation mechanism at longer reaction times and under more variable reaction conditions.

CONCLUSIONS

Oxidation of aromatic compounds was found to produce similar highly-oxidized molecules as has been found previously in monoterpene oxidation investigations. In experiments where dry ammonium sulfate seed aerosol was added to the chamber, it was shown that a large fraction of generated aerosol mass could be attributed to the HOM compounds that were directly detected from the reacting gas mixture.

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IMPACT OF ANTHROPOGENIC POLLUTANTS ON THE FORMATION AND FATE OF HIGHLY OXIDIZED MULTIFUNCTIONAL COMPOUNDS (HOMS) FORMED FROM THE OZONOLYSIS OF a-PINENE

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KEYWORDS: HOMS, MASS SPECTROMETRY, AEROSOL ACIDITY, HETEROGENEOUS CHEMISTRY.

INTRODUCTION

The largest mass fraction of atmospheric fine particulate matter (PM$_{2.5}$, aerosol with aerodynamic diameters ≤ 2.5 μm) 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 a-pinene are the major SOA precursors. Chemical characterization of gas- and particle phase products generated from the oxidation of a-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, I$^-$ and/or nitrate (NO$_3^-$), have however, 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 secondary organic aerosol (SOA).

Formation of HOMs has been proposed to occur through RO$_2$ chemistry and subsequent intramolecular hydrogen-shifts followed by rapid reaction with O$_2$ (Rissanen et al., 2015). 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 (Berndt et al., 2015).

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$_2$ + 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 might be expected. Indeed, multiphase chemistry of HOMs could be expected since it was recently highlighted that oxygenated species such as epoxides (Surratt et al., 2010) and/or organic hydroperoxides (Mutzel et al., 2015) undergo further multiphase reactions leading to SOA formation, highly oxidized compounds and/or volatile species. Therefore, once HOMs condense/uptake onto aerosol particles, they could re-evaporate, decompose or react with oxidants or other SOA constituents. It is worth noting that HOMs formed from the oxidation of a-pinene are expected to contain hydroperoxide (Ehn et al., 2014) and/or epoxide (Paulot et al., 2009) functional groups, and are likely to be reactive in the presence of acidified particles.

In this study we investigate the a-pinene ozonolysis in different NO regimes in the presence of sulfate seed aerosol of varying acidity with a focus on the formation and multiphase reactions of HOMs.

METHODS

The COALA-1 campaign was conducted at room temperature (26 ± 2°C, ~ 30% of relative humidity) 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 (O3, NO) and particles were continuously added to the chamber. Under the conditions used in this study, the average residence time in the chamber was ~ 40 min. Gaseous multi-functional organic compounds were chemically characterized using a range of time-of-flight chemical ionization mass spectrometers (HR-ToF-CIMS) with iodide (I−) and nitrate (NO3−) ionization. In addition, particle-phase was chemically characterized using Filter Inlet for Gases and AERosols (FIGAERO) coupled to an I−-HR-ToF-CIMS. Ozonolysis of α-pinene was systematically examined with varying VOC (1-30 ppb), ozone (10-100 ppb) and NO (0-10 ppb) concentrations. Ammonium sulfate aerosols (acidified and non-acidified) were also injected to further evaluate heterogeneous oxidations of HOMs. Non-acidified seed aerosol was generated from 0.06 M ammonium sulfate ((NH4)2SO4 (aq)) solutions and acidified seed aerosol from (NH4)2SO4 (aq) + 0.06 M H2SO4 (aq) solutions.

RESULTS

Preliminary results obtained from COALA-1 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, presence of NO impacts the RO2 chemistry and leads to the formation of organonitrates and alkoxy radicals. Even at large concentration of NO (up to ~ 2-3 ppb) HOM monomers, even though reduced, remain formed suggesting that RO2 intramolecular hydrogen-shifts reactions occur even in the presence of subsequent concentration of NO.

Organic hydroperoxides, HOMs, and/or oligomeric compounds such as those identified from the α-pinene ozonolysis, are important species in the atmosphere and are likely involved in SOA formation. However, the fate of such compounds (gas-particle partitioning, photolysis, reactive uptake, etc) is complicated and still remains unclear. Figure 1 presents the time series of selected HOMs formed from the ozonolysis of α-pinene in the presence of NO (2-3 ppb, steady-state concentration).

Figure 1. Times series of C10H14O4−11 formed from the ozonolysis of α-pinene in the presence of NO. AS and ABS correspond to the injection of non-acidified and acidified seed aerosol, respectively.

In the presence of non-acidified (NH4)2SO4 seed aerosols, condensation/reactive was observed for some of the identified compounds. HOMs are expected to have low vapor pressures (Ehn et al., 2014) that allow them to condense onto seed aerosol. The presence of acidified particles significantly enhanced the reactive uptake of these compounds. These preliminary results indicate that certain HOM monomers such as
C_{10}H_{16}O_{7,9} or C_{10}H_{16}O_{7,9} might contain an epoxide functional group. Presence of such functional group likely explains the large reactivity of these identified HOMs (Gaston *et al.*, 2014; Riedel *et al.*, 2015). Finally, identified organonitrates from the ozonolysis of α-pinene do not significantly uptake/condense onto either acidified or non-acidified seed particle. This result suggests that such compounds might be more volatile and/or they might have a weaker reactivity compare to oxygenated HOMs.

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NEW OPENINGS AT ATMOSPHERIC SCIENCE EDUCATION

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Keywords: HIGHER EDUCATION, MULTI-DISCIPLINARY, PEDAGOGY, CLIMATE CHANGE, AIR QUALITY.

INTRODUCTION

The society is facing Grand Challenges, such as climate change and air quality problems that require new education strategies. Traditional discipline oriented sectoral approach is not enough, but multidisciplinary approach combining knowledge from different disciplines and penetrate though all levels of society is needed. It is also not enough to educate degree students, but everywhere in a changing society there is urgent need to update knowledge based on the new scientific findings. The Finnish government’s strategic key project Knowledge and education aims at this with Action plans (Government Publications, 2016) combining higher education with continuing education and fostering at digital learning platforms and distribution of best practices for novel digital learning methods and combining knowledge from different disciplines and sectors.

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. We have realized that the 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). Therefore have suggested a model to improve the learning outcomes in multidisciplinary atmospheric science (Lauri et al., 2016) and present the principles shortly here. It is based on our experiences organizing more than 50 research-intensive short courses and other multidisciplinary course over the past 20 years. We also present two new multidisciplinary openings at atmospheric science education: Introduction to Modern Atmospheric Science I – look on Air Quality in China and the Finnish Universities’ joint course Climate.now, supported by Finnish Innovation Fund Sitra.

THE ATMOSPHERIC SCIENCE PARADIGM AND HORIZONTAL LEARNING

Atmospheric science courses themes typically overlap several traditional disciplines and also have participants (students, postdoctoral researchers, professors and other senior researchers) from several disciplines. In Figure 1, each triangle represents one discipline, here we have chosen four disciplines – physics, chemistry, meteorology and biology – as an example case. Each one of the triangles can be seen as a pyramid representing the learning of the methodologies and concepts of that particular discipline – the paradigm.
During a research-intensive short course the learning happens and new ideas arise in the shaded centre of Fig. 1, where the tops of the pyramids meet.

Horizontal learning uses expertize of participants from different disciplines and background and uses the heterogeneity of the students as an asset. We have adopted horizontal learning as a broader approach, addressing a cross-section of knowledge from different fields and blending the information to reach new levels of understanding (see Fig. 2). This horizontal learning principle has been shown to be a good example of participatory action research (Hennessy and Murphy, 1999).

Horizontal learning can be peer learning of students of different background also teachers can learn during the course both from colleagues and from interaction with the students.

Climate.now is a multidisciplinary study and teaching module on the basics of climate change that was published online at www.climatenow.fi on 12 September 2016. It contains written material, video lectures and interviews, assignments, tests and a guide for teachers. Using the material a higher education teacher can give a 5 ECTS course on the basics of climate change at his/her higher education institution. Material is aimed to students of all fields and is open to everyone. It means that it is open to everyone who wants to familiarise themselves with the basics of the climate change. The material can also be used by companies,
other organisations and the media. Climate.now answers the societal need to improve climate change education in higher education in Finland (Liljeström and Monni, 2015).

The course is organized as blended learning using University of Helsinki Massive Open Online Course (MOOC) platform, contact teaching and student study groups facilitating horizontal learning and peer support. The course material is multidisciplinary from climate change as a natural science phenomena to the impacts and adaptation as well as different mitigation strategies (inner circle in Fig. 3). Students are encouraged to deepen to the questions of their own field (outer circle in Fig. 3).

Figure 3. Climate.now education content and multidisciplinary questions surrounding it.

The material has been produced by the University of Helsinki, Lappeenranta University of Technology, Metropolia University of Applied Sciences and the Finnish innovation fund Sitra, in collaboration with the Finnish Meteorological Institute, Climateguide.fi, the University of the Arts Helsinki and the Ministry of Education and Culture. The multidisciplinary team consisted of natural scientists, behavioral scientists, engineers and artists.

We are planning to complement Climate.now e.g. by teachers’ training and peer support networking.

LOOK ON AIR QUALITY IN CHINA

The course has been given as Introduction to Modern Atmospheric Science I (IMAS I) – look on China at the University of Helsinki and it introduces modern research in atmospheric science with focus on air quality and a view on the current situation in rapidly developing China. The course covers air pollution from sources, transport and transformation, monitoring and remote sensing, modeling emissions, to
impacts on human health and ecosystem and ends with societal aspect of air quality, urbanization, societal
impacts and policy making.

The themes covered include air pollutants and their main sources; basics of meteorological transport;
chemical and physical transformation of pollutants, aerosol formation, coagulation and deposition
processes; exposure and health impacts of main pollutants; ecosystem responses to air pollution;
monitoring of pollutants and definition of air quality index; remote sensing methods and use of online
databases; air pollutants direct and indirect ecosystem and societal impacts; use of policies and
possibilities of urban planning in solving air quality problems.

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The atmospheric science paradigm and horizontal learning: experiences from short research-intensive


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AN ENERGY BALANCE PERSPECTIVE ON REGIONAL CO₂-INDUCED TEMPERATURE CHANGES IN CMIP5 MODELS

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Keywords: CLIMATE CHANGE, CLIMATE MODEL, ENERGY BUDGET, CMIP5.

INTRODUCTION

Changes in surface temperature are directly linked to changes in the surface and atmospheric energy budget. Here, this connection is analysed for climate models participating in the fifth phase of the Coupled Model Intercomparison Project, CMIP5 (Taylor et al., 2012). This research is reported in more detail in Räisänen (2016).

DATA SET

Output from 16 CMIP5 models is analysed. For each model, two idealised simulations are used: a control simulation with constant external conditions and a transient greenhouse simulation in which atmospheric CO₂ increases 1 % per year compounded. Climate changes are defined as time mean differences between these simulations over a 60-year period centred at the doubling of CO₂ (years 41-100). In addition to surface air temperature, total cloudiness and various top-of-the-atmosphere and surface energy flux components (but no three-dimensional model data) are used in the analysis (Räisänen, 2016).

METHOD

To a very good approximation, the simulated temperature changes ($\Delta T$) are decomposed into six main components

$$\Delta T = LW_{\text{CLEAR}} + SW_{\text{CLEAR-ATM}} + SW_{\text{ALBEDO}} + CLOUD + SURF + CONV$$

(1)

Here $LW_{\text{CLEAR}}$ represents the change in the clear-sky greenhouse effect, implicitly incorporating the direct CO₂ forcing and the water vapour and lapse rate feedbacks. $SW_{\text{CLEAR-ATM}}$ is mainly due to larger clear-sky short-wave absorption by increased CO₂ and water vapour, while $SW_{\text{ALBEDO}}$ incorporates changes in surface albedo. $CLOUD$ approximates the cloud feedback. $SURF$ represents the change in the net surface energy flux; for annual mean temperature changes this term is only important over the oceans. Finally, $CONV$ is the contribution from changes in horizontal atmospheric heat convergence (minus changes in local atmospheric energy storage, which can be neglected in annual mean analysis). Further details are given in Räisänen (2016).

RESULTS

A summary of the annual mean results is given in Fig. 1. The left column shows the 16-model means of temperature change and its six main components. On the right, the same decomposition is conducted for the inter-model standard deviation of temperature change (Eq. (10) in Räisänen 2016).
Figure 1. Simulated annual mean temperature change $\Delta T$ (row 1) and its decomposition (rows 2-7). Left: multi-model means. Right: the inter-model standard deviation of $\Delta T$ and the contributions of the individual components to it. The global area means are given in the top-right corner of the panels.
Focusing first on the multi-model mean changes, the following is observed:

- The global annual mean warming of 1.82 K is dominated and actually exceeded by $LW_{\text{CLEAR}}$. There is also some similarity in the geographical patterns, presumably mainly because water vapour increases more in areas with larger warming.
- $SW_{\text{CLEAR-ATM}}$ and $SW_{\text{ALBEDO}}$ both slightly enhance the global mean warming. While $SW_{\text{CLEAR-ATM}}$ is relatively evenly distributed, $SW_{\text{ALBEDO}}$ is regionally much more important in areas where sea ice and snow cover retreat, most notably the Arctic Ocean and the Tibetan plateau.
- $CLOUD$ makes a negative contribution in most of the world, but this is an artefact of the methodology. As discussed in Räisänen (2016), increases in CO$_2$ and water vapour tend to make the long-wave cloud radiative effect less positive where cloud cover remains unchanged. Despite this negative bias, there are areas where $CLOUD$ contributes to warming, for example over the eastern tropical Pacific, the Arctic Ocean, and much of Europe and Siberia.
- $SURF$ and $CONV$ are both locally very large (up to ± 6 K or even more) over the oceans, but exhibit a strong tendency of cancellation. Still, a comparison between Figs. 1a and 1k shows that the regions of small warming over the northern North Atlantic and the Southern Ocean are associated with a negative contribution from $SURF$ (i.e., reduced heat flux from the ocean to the atmosphere), whereas the maximum of warming in the Barents Sea coincides with strongly positive $SURF$. Thus, the pattern of temperature changes over the oceans is strongly regulated by $SURF$, although $CONV$ tends to smooth out its influence. Globally averaged, the contribution of $SURF$ is negative (-0.39 K or -0.53 K for oceans alone) because of net ocean heat uptake during a transient increase in radiative forcing.
- As expected, $CONV$ makes a near-zero contribution to the global mean temperature change. On the average, however, it is slightly positive over the oceans (0.12 K) and negative over the continents (-0.28 K). In essence, reduced horizontal energy transport from the oceans to the continents acts to spread out the effects of the net ocean heat uptake from sea to land areas.

Turning to the right column of Fig. 1, several conclusions can also be drawn on the energetic origins of inter-model differences in temperature change:

- Overall, the largest inter-model differences in warming occur at high latitudes, particularly the Arctic and Antarctic Oceans (Fig. 1b)
- On the average, the largest contributors to the inter-model differences are $LW_{\text{CLEAR}}$, $CLOUD$ and $SURF$. $SW_{\text{ALBEDO}}$ is of intermediate importance, whereas $SW_{\text{CLEAR-ATM}}$ is nearly negligible.
- The relative importance of the different terms varies with region. As illustrated in Fig. 2, $LW_{\text{CLEAR}}$ makes the single largest contribution to the inter-model differences in many land areas and the Arctic Ocean (34% of the globe). $CLOUD$ is commonly the dominant contributor particularly over low-to-mid-latitude oceans (29% of the globe) and $SURF$ over many higher-latitude sea areas (20% of the globe).
- In contrast to the other terms, $CONV$ mostly acts to reduce the inter-model differences in temperature change, particularly over the oceans (Fig. 1n). Changes in horizontal atmospheric energy flux convergence mostly act as a diffusion-like process, smoothing out spatial and, therefore, inter-model differences in temperature change. Nevertheless, $CONV$ acts to amplify the differences in warming over some regions, e.g. Greenland and Antarctica. This suggests that the magnitude of warming over these ice sheets is substantially controlled by heat transport from the surrounding oceans, where inter-model differences in warming are very large. Another area where $CONV$ amplifies the inter-model differences is Amazonia.
An energy balance decomposition was conducted for CO$_2$-induced temperature changes in an ensemble of 16 CMIP5 models. The results show that both the multi-model mean warming and the inter-model differences in warming are affected by several energy balance terms, the importance of which depends on the area (and season, see Räisänen 2016) considered. As the method only requires two-dimensional model data at the surface and the top of the atmosphere, it is relatively cheap in terms of its data needs and is therefore convenient to apply even to large ensembles of climate model simulations.

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Fog deposition measurements inside tropical rainforest in Taita hills, Kenya

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Keywords: FOG DEPOSITION, KENYA

INTRODUCTION

Fog deposition is an important part of the water budget of tropical montane cloud forests. These forests cover 1.4 % of total area of the world’s tropical forests (Bruijnzeel et al., 2011). The capturing of fog water and reduced erosion due to high infiltration capacity of the soils are the key hydrological functions of cloud forests. The tropical montane cloud forests are biodiversity hotspots with high degree of species endemism.

To understand the fog deposition in tropical montane cloud forests, we measured fog deposition and throughfall in two hilltop forest fragments in Taita hills, Kenya (3°25′ S, 38°20′ E). The fog deposition measurements were compared to the standard meteorological measurements. Througfall measurements during the fog events were compared to the throughfall amounts during rainfall events to understand the importance of fog deposition for the forest hydrology.

METHODS

The fog collectors were made according to the commonly used net type of fog collector (Schemenauer and Cereceda, 1994). It has a 1 m² square panel which has a double layer of Raschel type shading net. Each fog collector was paired with a tipping bucket rain gauge which was measuring rainfall or throughfall depending on the location of the collector. The fog deposition and rainfall amounts were logged every 30 minutes. The fog deposition measurements during rainfall were not used due to part of the rainfall is captured by the fog collector.

The fog collectors were placed along transect from the eastern slopes of the Ngangao forest to the western slopes (Figure 1). The weather station measuring temperature, relative humidity and wind speed and direction was located next to the fog collector FogN4OP at a small open space inside the forest. Weekly throughfall measurements were done using 25 buckets arranged in grid next to the FogN3FP.

Figure 1: The fog collectors are numbered starting from the western slope. The fog collectors with the letter O in their name are located on open space whereas with the letter F are located inside the forest. The wind rose shows distribution of wind at the western slope at the collector Fog4OP.
RESULTS

The annual precipitation at a nearby the Ngangao forest was 842 mm between September 2013 and August 2014. There are two major wet seasons: one in December and the other from February to April. There are distinct fog deposition events when no rainfall is present (Figure 2). The fog deposition at open space is higher than inside the forest. At the beginning of November, the fog deposition is high and the daily minimum relative humidity is increasing but this is not a general pattern. The daily mean wind speed did not show clear relation with fog deposition amounts, although the fog deposition efficiency of a net type of fog collector depends on wind speed (Frumau et al., 2011).

Figure 2: Cumulative sum of fog deposition and rainfall/throughfall, daily minimum relative humidity, daily average wind speed and daily maximum incoming solar radiation.
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REFERENCES


MODEL OUTPUT STATISTICS METHOD PERFORMANCE IN CHANGING CLIMATE: HYDROLOGICAL MODELING PERSPECTIVE WITH THE HYPE MODEL

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Keywords: MOS, CLIMATE MODELLING, HYDROLOGICAL MODELLING.

INTRODUCTION

Before global (GCM) and regional (RCM) climate model output can be used in hydrological climate change impact studies, they usually need to be adjusted for biases in relation to the observed climate. The so-called model output statistics (MOS) is a group of methods commonly used for such adjustments. The relative performance of MOS methods in construction of climate projections and their application in hydrological modelling studies has been documented in several publications. However, most of these studies have been constrained to the present-day and historical climate, as direct information of future climate is not available. An approach to make inferences on the relative MOS method performance in future climate is to use model simulations as surrogates for future climatic conditions. This so-called pseudo reality approach has lately gained more popularity in climate studies, but very few attempts have been made to apply the pseudo reality approach in the hydrological impact modelling step (e.g. Velázquez et al. 2015). To fill this gap, we test whether further information on the applicability of MOS methods in future climate can be gained from the hydrological modelling point of view. The aim is to compare a set of MOS methods using two pseudo reality approaches both in climate and hydrological modelling steps and to analyse how various hydrological aspects are affected by the differences between the MOS methods in different climatic conditions.

METHODS

Hydrological simulations were made using the Hydrological Predictions for the Environment (HYPE) model (Lindström et al., 2010) developed by the Swedish Meteorological and Hydrological Institute. HYPE is process-based, semi-distributed model designed for hydrological simulations at different spatial scales. To sample different climatic conditions, catchments from locations in Europe were selected from the European scale application E-HYPE 2.1 (Donnelly et al. 2016) based on the ability of HYPE to capture the observed hydrological conditions. Here, the results for the upper Tornio river catchment are discussed. To keep the model experiments simple, only daily mean temperature and precipitation are used as input to HYPE. Hydrological simulations were performed for years 1981-2010 and the end of the 21st century (2061-2090). Six GCM-GCM simulations, all having different driving GCM and RCM components, were selected from the CORDEX data base (Jacob et al. 2014) as future forcing data for HYPE. These simulations cover the European region and have been run with 0.11 degree resolution using RCP4.5 emission scenario forcing.

Daily mean temperature and precipitation projections are constructed using quantile mapping applied both in the delta change (DC) and bias correction (BC) mode. In the delta change mode, the observed time series are adjusted with the GCM-RCM simulated climate changes, while in the bias correction mode the future GCM-RCM simulations are corrected based on the differences between the simulated and observed climate in the baseline period. The implementation details are described in Räisänen and Räty (2013) and
Räty et al. (2014). Each day of the year was adjusted separately using 30-day window in the estimation of climate changes for DC and model biases for BC.

The pseudo reality tests are performed in the following manner. Each GCM-RCM at its time is selected as the pseudo reality against which the adjusted projections are constructed using the rest of the models and validated using proper statistical measures. This procedure is repeated for all model permutations (i.e., cross-validated) and the results averaged over all pseudo realities. The same procedure is applied also for the hydrological simulations using the MOS-adjusted projections as input. In their traditional form (hereafter, denoted as PS1) the pseudo reality tests, however, can potentially give misleading results from the hydrological perspective if GCM-RCM biases are substantial in the present-day climate, as HYPE (and any other similar hydrological model) has been calibrated using observations from the current climatic conditions. Thus, we also tested an alternative approach, where the GCM-RCM acting as pseudo reality was first corrected using the ERA-interim re-analysis adjusted with the WATCH forcing data methodology (Weedon et al., 2014) before performing the cross-validation and running the hydrological simulations (hereafter, denoted as PS2).

Several cross validation statistics can be used. Here, we show the mean squared error calculated over the quantiles of the pseudo reality and the predicting distributions \( f_{\text{pseudo}}(x) \) and \( f_{\text{pred}}(x) \), \( x = 0 \ldots 100\% \) as

\[
MSE = A \left[ \left( \frac{f_{\text{pred}}(x)}{\langle f_{\text{pseudo}}(x) \rangle} - f_{\text{pseudo}}(x) \right)^2 \right] 
\]

, where \( \langle \cdot \rangle \) denotes the average of either the five climate projections or hydrological simulation and \( A \) the average over all quantiles, 12 months, catchment area and the six pseudo realities.

RESULTS AND CONCLUSIONS

Figure 1. Cross-validated MSE in the years 2061-2090 for the uncorrected model simulations (raw) and the two MOS methods. The left panel shows the results for daily mean temperature (light grey) and precipitation (dark grey) and the right panel for total runoff. The bars denote the results obtained with PS1, while the statistics for the alternative pseudo reality approach (PS2) are denoted by the open circles.
The left side of Fig. 1 shows the MSE for daily mean temperature and precipitation in the upper Tornio river catchment in years 2061-2090. When comparing the results for PS1 (bars) and PS2 (open circles), it is seen that the differences in MSE are small between the pseudo reality approaches. Also the relative performance of DC and BC are very similar for both pseudo reality approaches. However, the MSE values of daily mean temperature are slightly larger for BC in PS2 and vice versa for precipitation. For the uncorrected simulations, the results are worse for PS2, indicating that the observed conditions are not completely covered by the selected GCM-RCMs.

The right panel in Fig. 1 shows similar statistics for total land-area runoff as simulated by HYPE. The statistics of the uncorrected simulations are substantially worse for the PS2, which was already seen for daily mean temperature and precipitation. On the other hand, the MSE obtained with PS2 is smaller for both methods than without the additional adjustment to the pseudo reality. In particular, the MSE for DC is noticeably smaller in this case and it performs slightly better in comparison to BC. This brief illustration suggests that the relative performance of the tested MOS methods is relatively similar in both pseudo reality approaches, although the DC method seems to have slightly better statistics in the hydrological modelling step. However, more study is needed to see whether the same conclusion holds also for other regions as well as different hydrological aspects, both of which are under research.

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STOMATAL AND NON-STOMATAL LIMITATION OF PHOTOSYNTHESIS

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Keywords: OSMOLALITY, TREE, STRESS, ECOPHYSIOLOGY, CARBON, WATER.

INTRODUCTION

Trees have to maintain a balance between carbon acquisition through photosynthesis (P) and water lose by transpiration (E). While water lose through transpiration is directly controlled by stomatal conductance ($g_s$), the regulation of photosynthesis is more complex and depends on light resources, and on the relation between leaf water and carbohydrates status (Paul and Penny 2003). While leaf water status is driven by transpiration controlled by $g_s$ in relation to the whole tree xylem water transport, the amount of carbohydrates is a function of photosynthesis (input) and phloem transport (output), which depends on autotrophic sink strength and xylem water relations (Nikinmaa et al. 2013). Therefore, photosynthesis is controlled by both stomatal and non-stomatal constraints, the latter resulting mainly from mesophyll resistance to CO\textsubscript{2} diffusion, photorespiration and oxidation activity of the RuBisCO.

Stomatal regulation of photosynthesis, particularly in relation to plant hydraulic status, has been extensively studied even if not fully understood yet. However, much less is known about non-stomatal constraints on photosynthesis. Studies in the recent years have hinted that mesophyll conductance can change rapidly and often amplify the effect of stomatal conductance response to environmental changes (Flexas et al. 2008). The biochemistry of photosynthesis has also been shown to have a diurnal dynamic (Guo et al. 2009). Furthermore, non-stomatal limitation has been shown to increase with leaf sugar concentration (Kitao et al. 2015). However, a general framework allowing to account for non-stomatal limitation of photosynthesis is still lacking.

Therefore, we aim to decipher the relative contribution of stomatal and non-stomatal limitation of photosynthesis across tree species by manipulating independently leaf water status and leaf osmolality (mainly driven by the amount of sugar).

METHODS

Potted saplings from \textit{Pinus sylvestris}, \textit{Picea abies}, \textit{Betula pendula} and \textit{Populus tremula} were used. Leaves or needles were enclosed in the measuring head of portable leaf-gas exchange measuring system (GFS-3000, Heinz Walz, GmbH, Effeltrich, Germany). Environmental conditions (e.g., light, temperature, humidity) in the measuring head were similar to those experienced by the rest of the sapling. Leaf gas-exchange and particularly P, $g_s$, E, leaf internal CO\textsubscript{2} concentration ($c_i$) were measured continuously during the course of the experiment.

After measurement of the gas-exchange baseline, saplings were either notched (removing part of the xylem to limit water supply) or girdled (removing of the phloem to stop phloem transport) to affect leaf water status – measured by its water potential – or leaf carbohydrate level – measured through leaf osmolality. Water potential was measured with a pressure chamber (1505D, PMS instrument company, Albany, OR, USA). Osmolality was measured with a freezing point osmometer (Osmomat-030, Gomotec, Berlin, Germany).

Similar measurements are currently performed on three controlled and three cold-girdled adult \textit{P. sylvestris} in Hyytiälä to test the applicability of our results on saplings in controlled conditions to full grown trees under field conditions. Cold girdling is achieved by circulating a water/ethanol solution close to 0°C in a tube wrapped around the tree trunk. Cold girdling is a fully reversible manipulation that leave the trees unharmed but temporarily impair phloem transport below-ground, leading to accumulation of sugars in the trunk above the girdling point and in the canopy. This experiment is still ongoing.
CONCLUSIONS

Under controlled conditions (constant light, VPD, etc.), the strongest response observed was of the ratio of photosynthesis over $c_i$ to changes in leaf osmolality (Fig. 1). Under our controlled conditions, we can assume that the effect of stomatal limitation of $P$ are accounted for by dividing $P$ by $c_i$, our result shows that accumulation of sugars impair photosynthesis. Furthermore, and more importantly, this relation holds across species and treatments. Therefore, our results suggest the limitation of C sink activity or impairment of phloem transport regulate photosynthesis in agreement with theoretical predictions (Hölttä et al. In revision).

![Figure 1. The relation between measured osmolality (osmo, in mol kg$^{-1}$) and photosynthesis divided by ci ($P_{ci}$, in mol air m$^{-2}$ s$^{-1}$) for the four studied species. The black line shows the regression (p<0.01) and the grey area show the 95% confidence interval. (Note that no actual data points are presented due to publication of the abstract in non-peer-reviewed venues.)](image)

However, the manipulations applied here are extreme. In field studies, conditions are not stable and $P$ is not solely responding to changes of $c_i$, our preliminary results show the best fit between leaf water potential – rather than osmolality – and gas exchange, including $P/c_i$. This suggest that stomatal limitation plays a central role under normal conditions. However, changes in leaf water status also appear to affect non-stomatal limitation, most likely the mesophyll conductance.

Therefore, our results show that under normal conditions, trees are able to regulate their gas-exchange mostly through their effective control of stomatal conductance. However, under extreme conditions (e.g., drought, intense herbivory) non-stomatal limitation are becoming central to tree physiology.

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carboxylation efficiency decrease and D1 degradation in bayberry (Myrica rubra) plants. Sci Hort 123: 188-196.
THE EFFECT OF REINDEER GRAZING ON SOIL FUNGAL COMMUNITIES AND ENZYME ACTIVITIES

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Keywords: BOREAL FOREST, FUNGAL COMMUNITY, PYROSEQUENCING, REINDEER GRAZING.

INTRODUCTION

Reindeers (Rangifer tarandus L.) are the most important large mammalian herbivores in northern ecosystems that graze freely in the Finnish Lapland. Currently there are approximately 1.5 reindeer per km² in the Finnish Lapland (Susiluoto et al. 2008, Köster et al. 2015).

By grazing and trampling reindeer affect plant diversity and coverage, soil nutrient cycling and soil organic matter decomposition. Changes caused by reindeer in vegetation (mostly in lichen coverage) have indirect effects on physical features of the soil e.g. soil microclimate, root biomass and also on soil carbon dynamics. Reindeers preferably eat lichens (e.g. Cladonia spp.) that in forested areas are often replaced by dwarf shrubs or mosses (Köster et al. 2015). In some areas, even bare soil can be exposed after overgrazing (Susiluoto et al. 2008) and it can increase soil temperatures and change soil moisture conditions (Stark et al. 2010, Köster et al. 2016). It has also been reported that the reindeer lichens (Cladonia spp.) can produce allelopathic extracts that inhibit development of mycorrhiza of Scots pine and dwarf shrubs (Brown and Mikola 1974), thus by removing the lichens reindeer can also affect soil fungal and microbial dynamics.

Our aim was to describe the fungal community composition in northern boreal subarctic forest soils grazed and non-grazed by reindeer, and estimate the overall effect of reindeer grazing on soil fungal communities. Further, our aim was to compare the fungal community structures to the decomposition rates and enzyme activities in grazed and non-grazed sites.

METHODS

Our study areas are located in the northern boreal subarctic coniferous forests, at the close vicinity of Sodankylä Arctic Research Centre of the Finnish Meteorological Institute and Värrö SMEAR I (Station to Measure Ecosystem-Atmosphere Relations) –station.

Soil sampling was conducted in 2013, and the soil samples (lower humus layer) for fungal community analyses were taken from four sampling areas, one located in Sodankylä and three in Värrö (Kotovaara, Nuortti I and Nuortti II). All areas had a fence that had excluded reindeer for approximately 60 (in Sodankylä and Kotovaara) to 100 years (Nuortti I and Nuortti II) and the samples were taken from both sides of the fence (grazed and non-grazed sides). In total, we had 38 soil samples from four locations, with 19 grazed and 19 non-grazed samples.
DNA was extracted from 0.2 g of humus soil with PowerSoil® DNA Isolation kit (MoBio Laboratories, Carlsbad, CA, USA) and purified with GeneClean Turbo –kit (MP Biomedicals, LLC, France). Fungal ITS2 region was amplified with the primers gITS7 (Ihrmark et al. 2012) and ITS4 (White et al. 1990) with appropriate pyrosequencing A- and B- adapters and unique 6 bp tag sequences attached. Pyrosequencing was done in the Institute of Biotechnology at the University of Helsinki. Pyrosequencing data was analysed with mothur pipeline v.1.31.2. (Scloss et al. 2009), following a standard operation procedure (Schloss et al. 2011). Sequences were trimmed, quality checked, aligned using pairwise alignment and clustered into operational taxonomic units (OTUs with 97% similarity).

Litter bags with Scots pine needles (approximately 5 g of material) were buried underneath the humus horizon to the same sample areas in Värriö in year 2014. Litter bags were harvested one year later, and 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-xylosidase, β-glucuronidase, cellobiohydrolase 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).

RESULTS AND CONCLUSIONS

Pyrosequencing of 38 soil samples yielded ~250 000 sequences that were classified into 1182 OTUs with 97% similarity. Overall, grazing did not have clear effect on fungal diversity or richness. Basidiomycota were the most abundant phyla in grazed and non-grazed areas, followed with Ascomycota and Chytridiomycota. Cortinarius was the most abundant genus in grazed and non-grazed areas, followed with Piloderma, Suillus and Lactarius. Even though on a phylum level grazing did not have a clear effect on fungal communities, on genus and species level, grazing clearly affected on certain genus and species.

On the other hand, enzyme activity measurements from the needle litter showed significant effect of grazing. In general, the enzyme activities were higher in the grazed sites compared to non-grazed sites, except laccase which was higher in the non-grazed sites. This indicates long-term changes in soil organic matter decomposition rate by the grazing.

Overall, even though reindeer grazing did not seem to have a clear effect on soil fungal community composition and diversity parameters, more in depth analysis revealed that some fungal genus and species were clearly affected by the grazing. Further, grazing also affected significantly on detected extracellular organic matter degrading enzyme activities and decomposition potential was higher on reindeer grazed areas.

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A COMBINATION OF SOURCE AND SINK EFFECTS DETERMINE THE GROWTH OF
SCOTS PINE ORGANS IN VARYING WEATHER CONDITIONS

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Keywords: PINUS SYLVETSIRIS L., TEMPERATURE RESPONSE, DYNAMIC MODELLING,
CARBON BALANCE.

INTRODUCTION

Trees have a clear annual cycle in boreal zone where they regulate the timing of growth to the favorable
season in summer. The metabolic status of a tree within the annual cycle can be described with the
concept of stage of development. The progress of the stage of development can be modelled as a function
of environmental factors (Hänninen and Kramer, 2007).

Environmental factors have a dual effect on growth as they affect both the rate of ontogenetic
development (indirect effect) and momentary growth rate (direct effect). Temperature is the most
important factor affecting growth and other processes in boreal zone (e.g. Hari et al., 1972). In addition
e.g. water availability (Hölttä et al., 2010) and day length (Caffarra and Donnelly, 2011) affect growth
timing and intensity. Temperature (or other factors) have been shown to have also delayed effects of one
or more years (Salminen and Jalkanen, 2005; Babst et al., 2013). Photosynthesis is the source of carbon
that is needed for growth, respiration and other purposes. Stored non-structural carbon (NSC) acts as a
buffer when the momentary rates of carbon assimilation and consumption are not equivalent (Palacio et
al., 2014).

Two opposite theories have been introduced about the factor that determines growth intensity: source and
sink limitation hypotheses. Source limitation hypothesis assumes that growth is limited by carbon
availability and thus the rate of photosynthesis determines the rate of growth (see Wiley and Helliker,
2012). Assimilated carbon is divided to the organs with some allocation pattern. In contrast, sink
limitation hypothesis assumes that environmental factors (temperature, moisture, light, nutrients)
determine the ability of tree organs to grow, which is described as sink strength (see Körner, 2015).
Photosynthesis or NSC storages are assumed to always be sufficient for covering the growth demand.

The purpose of this study was to define the effects of temperature on Scots pine growth at different
temporal scales and to estimate the relative importances of the source and sink effects on growth. For that,
we constructed a dynamic growth model CASSIA (Carbon Allocation Sink-Source InterAction) (Schiestl-
Aalto et al., 2015).

MEASUREMENTS

The study site at the SMEAR II (Hari and Kulmala, 2005) is a Scots pine stand established by sowing in
1962. It is located in southern Finland on a medium fertile site, classified as Vaccinium type. In 2012, the
dominant height and mean stem diameter at 1.3 m were 17.5 m and 19.6 cm, with density of 700 stems
ha⁻¹. In 2002, the stand was partly thinned from below decreasing the stand basal area from 24.3 m² ha⁻¹
to 17.9 m² ha⁻¹ on the thinned area.

GPP was derived from the ecosystem net CO₂ exchange (closed-path eddy-covariance system, Vesala et
al., 2005, Kolari et al., 2009). Temperature, precipitation and soil water content were measured at 1 – 15
min intervals and averaged to daily values.
Shoot and needle lengths were measured 3-5 times per week from 6-33 shoots during the growing seasons 2002-2012. The number of tracheids in each xylogenesis phase was measured from microcores taken from four trees 1 – 2 times per week during growing seasons 2007-2010 (Kalliokoski et al., 2012, Jyske et al., 2014). In addition, the annual ring width and height increment of the main stem were measured for years 1997 – 2011 by 29 increment cores and for years 1997 – 2012 by the distance between whorls of branches in 7 trees, respectively (Schiestl-Aalto et al. 2015). Needle length growth was measured during early growing seasons 2012, 2014 and 2015 to detect the threshold temperature for growth onset.

THE MODEL

The model calculates carbon assimilation and use for growth and respiration with a daily time step. The state variables of the model are stored carbon, and carbon in needles, roots and primary and secondary wood (Fig. 1). The formation of secondary wood is further divided to cell division, enlargement and wall formation.

The source i.e. photosynthesized carbon (measured GPP) is directed to carbon storage from which the sinks (respiration and growth) drag the needed carbon (Fig. 1). Maintenance respiration rate for each organ is calculated as a function of temperature and organ size with organ-specific parameters determined from chamber measurements. Growth respiration, on the other hand, is proportional to growth only (Penning de Vries, 1974). The potential growth rates of the four organs (sink strength) are calculated as:

$$\frac{dx_i}{dt} = f_i(s(t))g_i(t)L_i$$

where $i$ is organ and $f(s(t)) \in [0,1]$ describes the dependence of growth on the stage of development, $s$, that is a function of accumulated temperature (Schiestl-Aalto et al. 2015). $g(t) \in [0,1]$ is the momentary effects of environmental factors (mostly temperature) and $L$ is the maximum growth rate of the organ. Carbon availability in the storage then determines the actualized growth i.e. if storage falls under a threshold level, the actualized growth rate is lower than the potential. Carbon source also affects the maximum growth rate parameter ($L$) at different temporal scales: previous late summer GPP for needles and shoots (Salminen and Jalkanen, 2007) and current year GPP for secondary growth (Babst et al., 2012).

Figure 1. Model structure. State variables are shown in green squares and carbon flows with black arrows. Environmental factors are presented with brown circles and inherent variables with blue diamonds. The red and blue arrows show source and sink effects, respectively.
RESULTS AND DISCUSSION

Our results on the needle growth show that lower temperatures than often proposed (3-10 °C by Körner, 1998; 5.6-8.5 °C by Rossi et al., 2007) are sufficient for growth onset. Temperature sum with threshold temperature + 1 °C (temperature sum accumulates when T > threshold) predicted most accurately the growth onset and early growth of needles during spring 2012, 2014 and 2015.

We were able to predict daily shoot growth rate with indirect (stage of development) and direct (instantaneous effect) effects of temperature (Fig. 2a). In addition, we observed that the temperature of warm previous late summer lead to enhanced length of the growth period (in temperature accumulation units) of shoots in the following year (Schiestl-Aalto et al. 2013).

We concluded that short-term growth variations in normal conditions are caused by variation in sink strength because we were able to predict the within year growth of primary and secondary growth and needles with temperature and without direct effect of photosynthesis or stored carbon (Figs. 2, 3). On the other hand source effects (GPP effect on maximum growth parameter, \( L \)) were needed to produce the between year variation in growth. The assumed dependencies between GPP of previous or current growing season and maximum growth rate led to reasonable estimates of between year growth variation (Fig. 4).

![Figure 2](image1.png)

**Figure 2.** Measured and predicted shoot length (A) and needle length (B). The black line represents 1:1 and the black dots the year that was used for parameter estimation.

![Figure 3](image2.png)

**Figure 3.** Measured (dots) and predicted (lines) number of enlarging, wall forming and mature tracheids (blue, red and black, respectively).
CONCLUSIONS

We conclude that growth is limited by a complex combination of sink and source effects (see also e.g. Guillemot et al., 2015). Furthermore, environmental factors affect growth at different time scales varying from instantaneous effects to delayed effects from previous year(s). More research is needed to identify the factors determining the carbon flows to different processes. In addition, the effects of water limitation (Mina et al., 2016) should be included in the model to examine the effects of possibly increasing drought events (Kellomäki et al., 2005) on tree carbon balance. We need to know the causalities (instead of correlations) behind the processes to be able to predict changes in growth and carbon balance in varying environmental conditions.

ACKNOWLEDGEMENTS

We acknowledge Eero Nikinmaa, Harri Mäkinen, Juho Aalto and Janne Korhonen for the within year growth measurements, Kourosh Kabiri and Janne Levula for the annual growth data and Pasi Kolari for GPP data. The financial support by the Academy of Finland Centre of Excellence program (project no 272041) and project ‘Multi-scale modelling of tree growth, forest ecosystems, and their environmental control’ (257641) are gratefully acknowledged.

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consistent with a combined source – sink limitation of growth: implications for modelling. 

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HOW DUAL-POLARIZATION RADAR OBSERVATIONS CAN BE USED TO VERIFY MODEL REPRESENTATION OF SECONDARY ICE

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Keywords: Secondary Ice, Dual-polarization radar, WRF, Microphysics.

INTRODUCTION

One of the major uncertainties in climate projections is due to feedbacks between clouds and radiation. One reason for this is that detailed microphysical observations of cloud properties are still somewhat limited and thus microphysical parameterizations which are implemented in both weather prediction and climate models are difficult to verify.

A challenge in microphysics is to account for the high number of ice particles observed relative to the number of ice nuclei. Rime splintering, also known as the Hallett-Mossop (H-M) process, is an ice multiplication process which may explain this discrepancy. Hallett and Mossop (1974) conducted laboratory studies which showed that during the riming process ice splinters can be ejected during the freezing of supercooled liquid particles under certain conditions: at temperatures between -8 and -3°C and when liquid droplets with diameters greater than 25\(\mu\)m are present. Thus, the ice particles produced by the H-M process should be needles (i.e. non-spherical), appear where temperatures are between -8 and -3°C and where supercooled liquid is present and be present in much higher concentrations than ice nuclei at these relatively warm temperatures.

The aim of this study is to show the dual polarization radar observations can identify regions where newly formed ice particles in the -3 to -8°C temperature region exceed those expected from primary ice production, and therefore, in conjunction with additional observations (microwave radiometer measurements, surface-based precipitation microphysics measurements and radiosonde soundings), can identify areas of secondary ice production. The second aim is to use these observations to ascertain if secondary ice production can be captured by a numerical weather prediction model and identify any limitations in the parameterization of this process.

METHODS

We analyze observations made during the 2014 Biogenic Aerosols — Effects on Clouds and Climate (BAECC) campaign (Petäjä et al., 2016) and combine these observations with results from a numerical weather prediction (NWP) model. The United States Department of Energy’s Atmospheric Radiation Measurement (ARM) Program ARM Mobile Facility (AMF2) was deployed to Hyytiälä for 8 months during the campaign. Here we focus on the 15–16 February 2014 snowfall case.

Observations from the Finnish Meteorological Institute Ikaalinen radar, which is a dual-polarized C-band weather radar, and the ARM Ka-band scanning cloud radar are analysed. Observations of equivalent reflectivity factor (\(Z_e\)), differential reflectivity (\(Z_{dp}\)), linear depolarization ratio (\(LDR\)), and specific differential phase (\(K_{dp}\)) are available. \(K_{dp}\) is helpful for identifying secondary ice particles as it is only sensitive to non-spherical particles. Thus elevated values of \(K_{dp}\) which
occur where the temperature is between -3 and -8°C and where super-cooled liquid is present is a strong indication of the H-M process. Analysis of the $K_{dp}$ signatures is supported by ground-level observations of the microphysical properties of snow particles measured with NASA Particle Imaging Package (PIP).

Model simulations were conducted using Weather Research and Forecasting (WRF) model (Skamarock et al., 2008) which consisted of an outer domain and three nested domains. We analyse output from the inner-most domain which has a horizontal grid spacing of 1 km. The double-moment Morrison microphysics scheme (Morrison et al., 2005) is used which predicts the mixing ratio of water vapor and five hydrometeor species (ice, snow, graupel, rain and cloud liquid) as well as the number concentration of ice, snow, graupel and rain particles. Secondary ice production due to rime-splinters is parameterized following Hallett and Mossop (1974). For the H-M part of the parameterization to become active the temperature must be between -3°C and -8°C, graupel must be being produced, and the collection of cloud water by snow or the collection of snow by rain must also be occurring. In addition, the snow mixing ratio must exceed $0.1 \times 10^{-3}$ kg kg$^{-1}$ and either the cloud water mixing ratio must exceed $0.5 \times 10^{-3}$ kg kg$^{-1}$ or the rain mixing ratio must exceed $0.1 \times 10^{-3}$ kg kg$^{-1}$. These ad-hoc values originate from Lin et al. (1983).

Sensitivity experiments (see Table 1) were conducted to investigate the impact of these ad-hoc thresholds and the primary ice parameterization. An experiment (HM10) in which the production rate of ice due to the H-M process was multiplied by a factor of 10 was also performed.

RESULTS

The dual polarization radar observations showed that high specific differential phase values were observed at 0030 UTC on 16 February directly above Hyytiälä (Fig. 1). The 00 UTC radiosonde sounding confirmed that these $K_{dp}$ values occurred in a layer where the temperature was between -3°C and -8°C and the microwave radiometer showed that super-cooled liquid was present in the

---

Table 1: Summary of experiments conducted with WRF.

<table>
<thead>
<tr>
<th>Exp. Name</th>
<th>Microphysics scheme</th>
<th>Primary Ice parameterization</th>
<th>$Q_{\text{rain}}$ / $Q_{\text{cloud}}$ thresholds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Morrison</td>
<td>Cooper curve on</td>
<td></td>
</tr>
<tr>
<td>DeMott</td>
<td>Morrison</td>
<td>DeMott curve on</td>
<td></td>
</tr>
<tr>
<td>No Thres</td>
<td>Morrison</td>
<td>Cooper curve off</td>
<td></td>
</tr>
<tr>
<td>DeMott + No Thres</td>
<td>Morrison</td>
<td>DeMott curve off</td>
<td></td>
</tr>
<tr>
<td>HM10</td>
<td>Morrison</td>
<td>Cooper curve off</td>
<td></td>
</tr>
</tbody>
</table>

---

Figure 1: RHI observations of specific differential phase. Vertical dashed lines indicate profiles above the measurement station.
Figure 2: Model simulated hydrometeors (shading) and temperature (contours) from the control simulation at the grid point closest to Hyttiälä between 18 UTC 15 February 2014 and 06 UTC 16 February 2014. (a) number concentration of snow particles ($N_{\text{snow}}$), (b) number concentration of cloud ice particles ($N_{\text{ice}}$), (c) sum of the cloud liquid and rain mixing ratio ($Q_{\text{cloud}}+Q_{\text{rain}}$) and (d) graupel mixing ratio ($Q_{\text{graupel}}$). Units in panels a–b are m$^{-3}$ and kg m$^{-3}$ in panel c–d. The black solid line show -15°C, the blue solid line -8°C, and the blue dashed line -3°C. Note that color bars differ between panels. (e) Number concentration of the sum of all frozen particles ($N_{\text{ice}}$, $N_{\text{snow}}$ and $N_{\text{graupel}}$) at the lowest model level (∼40 m) in all experiments.

column at the same time (not shown). Furthermore, surface-based PIP observations of particles size, shape and velocity showed that three types of particles were observed: small needles, aggregates and rimed particles. Rimed particles are required for the H-M process to occur, the small needles are an expected product of the H-M process and the aggregates are thought to form from the newly produced needles. In addition, the PIP observations showed that an order of magnitude more needles are observed at the surface than primary ice parametrizations would account for and scattering calculations showed that ice concentrations must exceed those of primary ice to explain the observed $K_{dp}$ values above the surface. Thus, we conclude that secondary ice was being produce by the H-M process.

In the control WRF simulation (Fig. 2), maximum ice concentrations of 23 m$^{-3}$ occur between 00 UTC and 01:30 in the layer where the temperature is between -8°C and -3°C. These values are similar in magnitude to what would be expected from the parameterization of primary ice production and are much lower than observed at the surface (Fig. 2e). Thus, although supercooled liquid (Fig. 2c) and graupel (Fig. 2d) was simulated by WRF in the layer where the H-M process was observed to occur, the ice particles simulated between -3°C and -8°C are not formed by the H-M parameterization.

In No Thres (Fig. 3, left column) much higher ice number concentrations (maximum value, 5.3×10$^3$ m$^{-3}$) are simulated between 23:30 UTC and 00:00 UTC at ∼2 km than in the control simulation. The model calculated ice number production tendencies due to the H-M process (not shown) confirm that ice was produced due to the H-M parameterization. In HM10, (Fig. 3, right column) even higher ice concentrations (maximum value, 4.9×10$^4$ m$^{-3}$) are simulated. In both the No Thres and HM10 experiments the number of simulated frozen hydrometeors was less than observed (Fig. 2e), although HM10 does produce much higher concentrations than No Thres and thus agrees best with observations. Changing the primary ice parameterizations had little impact on the number of frozen hydrometeors simulated near the surface (Fig. 2e) or in the -8°C to -3°C layer (not shown).
Figure 3: Model simulated hydrometeors (shading) and temperature (contours) in experiment No Thres (left) and HM10 (right). (a,b) number concentration of snow particles ($N_{\text{snow}}$), (c,d) number concentration of ice particles ($N_{\text{ice}}$), (e,f) sum of the cloud liquid and rain mixing ratio ($Q_{\text{cloud}} + Q_{\text{rain}}$) and (g,h) graupel mixing ratio ($Q_{\text{graupel}}$). Units in panels a–d are m$^{-3}$ and kg m$^{-3}$ in panel e–h. The black solid line show -15°C, the blue solid line -8°C, and the blue dashed line -3°C. Note that color bars differ between panels.

CONCLUSIONS

Dual-polarization radar observations, which are now available from operational radars, can be used to detect zones where secondary ice production may take place. The results of this study suggest that current operational NWP models cannot realistically represent secondary ice. However, only one case was considered and therefore the validity of these results should be further investigated.

ACKNOWLEDGEMENTS

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Towards Robust Data Selection Criteria to Study Aerosol-Cloud Interaction

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Keywords: Aerosol-Cloud Interactions, Biogenic Aerosols, Boreal Forest.

Introduction

Aerosol-cloud interactions (ACI) remain in focus of many research groups due to the high complexity of involved processes and lack of collocated long-term measurements of aerosols and clouds. Meteorological drivers and state of boundary layer affect cloud formation and existence and, therefore, pose difficulties in attributing changes of observed cloud properties to the modification in aerosol loading. It is expected that concentration of biogenic secondary organic aerosol (BSOA) formed in the boreal forest environment will increase due to the growing temperatures and enhanced emission of precursor vapors by plants. BSOA can grow to the cloud condensation nuclei (CCN) sizes and participate in cloud processes, particularly in low-level warm clouds.

Aerosol-cloud interactions do not stop with CCN activation: cloud droplets growth, dry air entrainment, aerosol scavenging and sedimentation occur simultaneously and should be taken into consideration when discussing observed correlations. Coupling/decoupling of clouds to/from the surface, updraft/downdraft motions, available for condensation moisture together control cloud processes. Careful data selection criteria must be applied before making conclusions on ACI. 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 collection of data that can be utilized to study ACI in the active BSOA formation zone. Warm low-level clouds were detected during five months (April-early September) throughout campaign time. Among collected parameters that we use to study ACI are surface aerosol properties, aerosol backscatter profiles, liquid water path (LWP), cloud phase, cloud vertical extent and precipitation occurrence.

Method and Results

In order to separate the effect of meteorological parameters from aerosols, we focus on investigating adiabatic liquid water content (LWC) gradient, dilution coefficient and cloud depth. Data shows that adiabatic LWC gradient, which depends only on the cloud base temperature and pressure, correlates with the CCN-sized aerosol concentration (Fig.1). This implies that these two parameters depend on a common factor, likely surface temperature. It is known that BSOA concentration and temperature correlate via precursor vapors emission dependency on the temperature. At the same time, temperature at the cloud base directly relates to the surface air temperature. If the data would not be binned based on these defining parameters, a “pre-selection” of the data favoring certain correlations would occur. The width of distribution of adiabatic LWC gradient, dilution coefficient and cloud depth will also be studied in detail. Comparing different air mass origins, coupled or decoupled clouds, updraft or downdraft regions, precipitating or non-precipitating cases will facilitate deep understanding of the collected data. We envision that the data classification scheme explored here will provide crucial information on the aerosol-cloud interactions in the boreal environment.
Figure 1. Probability distribution function of adiabatic liquid water content gradient shown for different concentrations of aerosols larger than 150 nm for clouds with cloud base situated within boundary layer (left panel) and above boundary layer (right panel). Only precipitating low-level warm clouds are considered.

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MODELLING SUN-INDUCED FLUORESCENCE AND PHOTOSYNTHESIS IN NORTHERN EUROPE

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Keywords: JSBACH MODEL, CARBON CYCLE, BOREAL FORESTS, REMOTE SENSING.

INTRODUCTION

It is important to assess the current terrestrial carbon sink and its distribution at global scale and understand its functioning, in order to make reliable estimates of future’s carbon cycle in changing climatic conditions. Land surface models (LSMs) are often used in making estimates of land net carbon balance (Sitch et al., 2015), but evaluating and improving their performance is a challenge especially at regional and global scales.

Recently, estimates of sun-induced fluorescence (SIF) have become available from satellites (e.g. Frankenberg et al., 2011, 2014; Guanter et al., 2012). The SIF signal originates from the photosynthetic apparatus of the plants, while they photosynthesize. SIF has been shown to relate better to GPP than other remote sensing indices (e.g. Frankenberg et al., 2011). This was true also for boreal coniferous forests (Walther et al., 2016), ecosystem type that usually poses a challenge for interpretation of remote sensing data (Böttcher et al., 2016).

In this work we implemented SIF model to JSBACH (Jena Scheme for Biosphere-Atmosphere Coupling in Hamburg) LSM and evaluated its performance against SIF signal retrieved from remote sensing data from GOME-2 (Global Ozone Monitoring Experiment-2). Our study focused in Finland and Fenno-Scandinavian region.

METHODS

Land Surface Model We used LSM JSBACH (Reick et al., 2013) that is part of the Max Planck Institute’s Earth System Model (Giorgetta et al., 2013). JSBACH calculates carbon, water and energy cycles taking place between the land surface and atmosphere. The photosynthesis formulation for C3 plants is based on Farquhar et al. (1980) and the stomatal conductance is from Knorr (2000). The vegetation is described by different Plant Functional Types and in our set-up each grid point can contain up to four different vegetation
types. There are four different phenology descriptions that control the yearly cycle of leaf area for all the vegetation types (Böttcher et al., 2016).

**Chlorophyll fluorescence model** The model calculating SIF is based on unpublished work by F. Magnani and C. Van Der Tol. It was adapted to the JSBACH with slight modifications. The SCOPE model (Soil-Canopy Observation of Photosynthesis and Energy) (Van Der Tol et al., 2009) was used in estimating the extinction of the SIF signal within the canopy.

**SIF observations from GOME-2** We used data from GOME-2 (Global Ozone Monitoring Instrument 2) to obtain estimates of SIF with approach of Köhler et al. (2015). GOME-2 is an operational medium resolution nadir-viewing spectrometer on-board EUMETSAT’s MetOp-A and B (Meteorological Operational Satellites) (Munro et al., 2006). The retrieved SIF was available for years 2007–2011 with spatial resolution of 0.5° x 0.5°.

**Regional scale simulations** The regional simulation was done for Fenno-Scandinavian region. The meteorological data for the simulation was prepared with the regional climate model REMO (Jacob and Podzun 1997, Jacob 2001, Jacob et al., 2001). The spatial resolution of the simulation was 0.1667 degrees and it was done on hourly resolution.

**Regional scale data** For comparison of the simulated GPP we used a GPP product from MPI-BGC (Max-Planck-Institute for Biogeochemistry). This product is data-based and has been up-scaled to global scale using model tree ensemble approach (Jung et al., 2009, 2011) and it is available monthly.

**RESULTS AND CONCLUSIONS**

The comparison between satellite-observed SIF and simulated SIF revealed similar spatial patterns in Fenno-Scandinavian region (Fig. 1a,b). These spatial patterns also coincided with the simulated GPP and regional scale GPP product (Fig. 1). The mountain region is a challenge for remote sensing observations. The satellite-observed SIF has somewhat stronger north-south gradient than the simulated SIF.

The modelled SIF signal had similar latitudinal dependency than the observed SIF signal from GOME-2 (Fig. 2a). In the observations the latitudinal region 58°-62° showed the largest spread of the regions in the averaged annual values. However, the GPP from the regional data product from this region was more concentrated on higher values (Fig. 2b). Overall, the modelled GPP values were at lower level than those of from the regional GPP product. Also, the simulations have lower values than 400 g C year⁻¹ in all other than the most southernmost region, whereas such low values were missing from the GPP data product. The spatial variability is anyhow similar between the modelled GPP and regional GPP product (Fig. 1c,d).

The implementation of SIF module in the JSBACH LSM was successful and both simulated and observed SIF signals showed ability to follow GPP in Fenno-Scandinavian region. This opens possibilities for use of the SIF in data assimilation in order to improve modelling of GPP. Practical applications include monitoring of disturbances in the forests, e.g. pests, and also with the help of modelling tools more in-depth knowledge of regional scale photosynthesis helps in estimation of biomass stock development.
Figure 1. The averaged remotely sensed SIF (a), simulated SIF (b), simulated GPP (c) and data product GPP (d) averaged for years 2007-2011. The magnitudes are scaled to the 90th percentile.

Figure 2. The remotely sensed SIF vs. simulated SIF (a) for different latitudinal regions averaged for 2007-2011. Data based GPP product vs. simulated GPP (b) for the same latitudinal regions and time period.
ACKNOWLEDGEMENTS

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COMPARISON OF THREE NATURE-INSPIRED METAHEURISTIC ALGORITHMS IN DETERMINING THE VOLATILITY DISTRIBUTION OF α-PINENE DERIVED SOA PARTICLES

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Keywords: α-pinene SOA, VBS, Optimization

INTRODUCTION

Secondary organic aerosols (SOA) are formed through the gas phase oxidation reactions of volatile organic compounds and their consequent gas-to-particle transition (Hallquist et al., 2009 and references therein). On a global scale atmospheric organic aerosols, of which large fraction is SOA, can account for as much as 20-90% of the sub-micron particulate matter (Jimenez et al., 2009 and references therein).

Atmospheric SOA formation involves complex chemistry and possibly thousands of individual compounds (Goldstein and Galbally, 2007). All the steps or even the species participating in the formation process have not been identified yet. It is shown, however, that especially aromatic compounds such as α-pinene can produce significant yields of SOA mass in the chamber experiments (e.g. Pathak et al., 2007). However, even for α-pinene derived SOA particles all the end products from the oxidation reactions are not known.

In the description of SOA particle composition, a volatility-basis-set (VBS) approach developed by Donahue et al., (2006) has been shown to be of practical use. In the VBS approach the myriad of chemical compounds involved are described through grouping them into a discrete set of saturation concentrations. For example Pathak et al. (2007) and Vaden et al. (2011) have determined and tested the volatility distribution for SOA particle in growth and evaporation experiments. They used a 7-bin VBS from $10^{-2}$ to $10^{4}$ μg m$^{-3}$ with decadal difference. Yli-Juuti et al. (2016) (see also the abstract by Yli-Juuti et al.) assumed that the SOA particles derived from α-pinene ozonolysis in chamber experiments behaved like a well-mixed liquid at the relative humidity (RH) of 80% and used a detailed kinetic model combined with a genetic algorithm (e.g. Goldberg, 1989) to find an optimal initial SOA particle composition which best fit their measurements using an 8-bin VBS from $10^{-3}$ to $10^{4}$ μg m$^{-3}$.

To model the evaporation of the SOA particles in experiments an input of the initial particle phase composition is given for the evaporation model which then simulates the evaporation dynamics for the given initial composition. To define an optimal initial particle composition, described by the VBS, a cost function defined as the squared sum of the residuals between the measured and modelled evaporation is minimized.

To calculate the global minimum of the cost function analytically the function's gradient with respect to the mass fractions of the VBS bins must be calculated. It is, however, often difficult or computationally inefficient to calculate the gradient of the cost function for models containing several parameters. One must thus rely on algorithms that do not need the information about the gradient to explore the parameter space. These algorithms are often heuristic in nature, meaning that the results obtained are often good for extracting quantitative information but there is no guarantee that the found set of input parameters are the optimal ones. This raises a need to test the performance of different algorithms on the same problem. In this work we compare the performance of the genetic algorithm used by Yli-Juuti et. al. (2016) to two other metaheuristic search algorithms which have been shown to out-perform genetic algorithms in some applications (Yang and Deb, 2009).
METHODS

We tested the performance of three algorithms (the genetic algorithm, the particle swarm optimization and the cuckoo search) in finding the best initial VBS to the RH80% evaporation results of Yli-Juuti et al. (2016). These algorithms are introduced below. Every method was run with a solution size of 100 and 14 iteration rounds or generations. We also assessed the optimal VBS distribution by randomly generating solutions 100 times per one set which serves as a base case for evaluating the algorithms. For every method 50 individual best solutions were produced by running the method with different initial solutions.

We used the same evaporation model as Yli-Juuti et al., (2016) keeping the other physiochemical parameters of the VBS compounds same. In the model the molar masses of each compound were set to \( M = 150 \text{ g mol}^{-1} \), the density to \( \rho = 1.2 \text{ g cm}^{-3} \) and the gas phase diffusivity to \( D = 0.058 \text{ cm}^{2} \text{s}^{-1} \) and in every simulation the wall losses of the chamber were assumed so high that any gas phase compounds were removed instantly from the gas phase onto the chamber walls.

The genetic algorithm (GA) (e.g, Goldberg, 1989) mimics the natural evolution observed in nature. In GA a population of solutions where each solutions contains the initial mass fractions of the VBS bins are first created randomly. After this two solutions are chosen to the crossover procedure where a new solution is created by combining the two chosen solutions according to a problem-specific breeding scheme. After the crossover a mutation is performed to the new solution with a predefined probability where the mass fractions of two bins are swapped randomly. The new solution is accepted to the new generation of solutions if the cost function, or fitness, of the solution is better than the worst fitness in the previous generation. If this is not satisfied in our algorithm one of the two chosen solutions is chosen to the new generation with equal probability. The algorithm creates new generations of solutions as long as a predefined number of generations have been created. In the genetic algorithm the number of free parameters are the population size, number of generations and the mutation probability.

The inspiration behind the particle swarm optimization (PSO) (Eberhart and Kennedy, 1995) comes from the behaviour of bird flocks or fish schools. In the PSO the swarm of solutions, called particles, are moved around the parameter space so that the next position of a particle is influenced by the current position, the best known position of the particle and the best known position of the whole swarm. In the computer implementation this is done by calculating the velocity by which the particle position (the mass fractions of the VBS bins) is changed between the iterations. This velocity is calculated as the differences between the current and the best positions weighted by a user-defined free parameters. The number of the particles, the times the particles position is changed, the value for the maximum velocity and the user defined free parameters for the velocity calculation gives a total number of six free parameters for the PSO algorithm used here.

The Cuckoo search (CS) (Yang and Deb, 2009) is inspired by the breeding behaviour of cuckoos who lay eggs to nests of other bird species. In nature the cuckoo's egg is found by the host bird if the egg does not resemble it's own eggs. CS is programmed so that the initial solutions, called nests, are first created randomly and in every iteration new nests are calculated from the previous ones by performing a Lévy flight. If the new nest corresponds to a smaller value of the cost function than the previous nest, the old nest is replaced by the new nest. After the generation of the new nests a predefined fraction of nests are discover and replaced by new solutions. In the CS implementation used here the free parameters are the number of nests, the number of iterations and the probability for the nest to be discovered.

RESULTS

Table 1 summarizes the comparison of the three algorithms (GA, PSO and CS) and the random method. From the table it can be seen that every algorithm behaves better than the random exploring of the parameter space but the differences are not remarkably high between any optimization method. In addition, figure 1 a shows the evaporation curves, that best fit the measured evaporation, produced by the
evaporation model with the initial particle composition optimized with the four methods listed in Table 1. All the modelled evaporation curves fit well to the experimental results taking into account the uncertainty in the measurements. However, the randomly generated solution performs worse especially in capturing the evaporation near the measurement point closest to the 50 minute mark. Figures 1 b-d show the distribution of the optimal initial VBS mass fractions from the 50 individual simulations produced by the three optimization algorithms. The distributions do not show clear difference and all indicate that the evaporation curve can be produced with varying initial compositions and there must be a significant fraction of mass in the two least volatile bins.

Table 1 lists also the number of the free parameters that the user must define for a given algorithm. The GA and CS have both 3 parameters whereas for the PSO total of 6 free parameters must be defined either by hand or through other optimization schemes. Given that performance of the three optimization algorithms presented here are similar, we conclude that for this particular problem the best course of action when choosing an optimization algorithm is to choose an algorithm which has the smallest number of free parameters. We also note that caution must be paid when tuning the free parameters of any metaheuristic algorithm for a given problem.

<table>
<thead>
<tr>
<th>Method</th>
<th>Free parameters</th>
<th>Average cost function of the best solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA</td>
<td>3</td>
<td>$(1.5 \pm 0.4) \times 10^{-3}$</td>
</tr>
<tr>
<td>PSO</td>
<td>6</td>
<td>$(2.2 \pm 0.7) \times 10^{-3}$</td>
</tr>
<tr>
<td>CS</td>
<td>3</td>
<td>$(1.8 \pm 0.3) \times 10^{-3}$</td>
</tr>
<tr>
<td>Random</td>
<td>0</td>
<td>$(5.3 \pm 3.8) \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 1. Comparison of the methods: the free, user defined, parameters associated with the method and the average value of the cost function for 50 individual simulations. Error in the average value is the $1\sigma$ limit.

Figure 1. a) Measured evaporation of the SOA particles at 80% RH and the best simulated evaporation curves with the initial VBS distributions optimized with GA, CS, PSO and randomly generated solutions. b-d) Distribution of optimal VBS distribution found with a given algorithm from the 50 simulations. The box limits show the 25-75 percentile range and the whiskers the minimum and maximum value found for a given VBS bin.
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Introducing UCLALES-SALSA: a large-eddy model with interactive sectional microphysics for aerosols, clouds and drizzle

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Keywords: Boundary-layer, cloud physics, wet deposition, aerosol-cloud interactions

INTRODUCTION

A cloud resolving model coupled with highly detailed interactive description for aerosol and cloud microphysics has been developed. The aim of this work is to reduce the uncertainty in aerosol-cloud interactions. Even though our understanding of the aerosol-cloud interactions and the aerosol indirect effects has improved during recent years, many aspects continue to impair especially the projections of the global climate. Some of these challenges are related to the impacts of cloud processes that feed back on the aerosol population, such as aerosol scavenging and wet deposition as well as cloud processing of aerosols due to e.g. collision-coalescence processes. In turn, significant shortcomings arise due to the complex coupling between microphysics and the boundary-layer and cloud dynamics. These factors typically amplify or attenuate the initial impact of aerosols on clouds, depending of the ambient conditions and forcings. For these reasons, the design of the UCLALES-SALSA targets especially the effects of in-cloud collision-coalescence and wet deposition on the aerosol size distribution, while also considering the feedbacks between microphysics and cloud dynamics. Test experiments with the new model, comprising the evolution of a marine stratocumulus case as well as a case featuring the development of radiation fog, have been performed and are presented here.

METHODS

The boundary-layer dynamics in the new model are described by the widely used UCLALES Large-Eddy Model (LEM). The core of the model is based on the Smagorinsky closure. The microphysics is based on the SALSA (Sectional aerosol module for large-scale applications; Kokkola et al., 2008) spectral bin aerosol model, previously used in the ECHAM climate model. During this work, SALSA has been extended for cloud droplets and rain. The bin layout of the model is shown in Figure 1. It follows a unique approach, where the system tracks the dry aerosol particle diameter for both non-activated and activated particles. This allows us to preserve as much information as possible about the aerosol size distribution upon cloud activation, scavenging and deposition processes. The extended SALSA includes all the important collision and condensation processes. Cloud activation is computed based on the resolved hygroscopic growth of the aerosol particles. In this work, we assume a simple sulphate aerosol population, although desert dust, organic and black carbon and sea salt could also be included in the simulations.

The model thermodynamics is described by prognostic liquid water potential temperature and total water mixing ratio (vapour + liquid). The microphysics of the default UCLALES is based on the scheme of Seifer and Beheng (2001) with predicted mass and droplet number for rain. The cloud droplet number is prescribed and the clouds are assumed to be in equilibrium through saturation adjustment. The UCLALES includes a simple four stream radiative transfer solver based on Fu and Liou (1993), which is used in this work.

The model is tested in two cases: one comprising a marine stratocumulus deck based on the DYCOMS-II RF02
and one comprising a radiation fog case at Cardington, UK. The stratocumulus case is initialized with the idealized initial sounding given in the model intercomparison work by Ackermann et al. (2009). Model experiments are performed with the UCLALES-SALSA and the default UCLALES (prescribed droplet number concentration, bulk microphysics). For the fog case, we initialize the model based on Porson et al. (2011) and compare the results on the observed data presented in Price (2011).

**CONCLUSIONS**

Compared to the default UCLALES, UCLALES-SALSA considerably changes the model dynamics and interpretation of the system evolution. For the stratocumulus case, drizzle formation in UCLALES-SALSA initializes a rather efficient scavenging and eventually wet deposition of aerosol, which starts to deplete the cloud activating particles. This changes the cloud radiative properties and thus entrainment, while drizzle modulates the boundary layer stability. The microphysical and dynamical impacts cause changes in the boundary-layer dynamics which yield a positive feedback loop. The results show a distinct transition from a mixed phase stratocumulus topped boundary-layer to a decoupled, very thin stratiform cloud layer below the main inversion. This is in significant contrast to the default UCLALES, where the simple microphysical description with prescribed droplet concentration effectively inhibits such a transition and the solid stratocumulus deck remains. In terms of the interpretation of the model results, this means that the UCLALES-SALSA natively produces a more transient evolution of the boundary-layer, reminiscent of a domain advected with the large-scale flow. In contrast, the default UCLALES assumes a constant resupply of aerosol particles by advection into the model domain.

In the case of fogs, we see that the UCLALES-SALSA is able to quite well reproduce the initiation and evolution of a radiation fog layer. Features such as the fog radiative heating profiles and the growth rate of the fog depth are well captured. Microphysical interactions, including the fog droplet activation due to the radiative flux divergence at the top of the fog layer are well captured. In particular, UCLALES-SALSA is able to

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*Figure 1: Schematic representation of the bin layout and processes included in the extended SALSA module. Aerosol and cloud droplet bins (green and light blue) are parallel with each other and follow the same size range for dry particle diameter (from 3 nm to 10 μm). In contrast, the drizzle bins (dark blue) are defined according to the wet diameter of the droplet and cover the size range between 50 μm and 2 mm.*
reproduce the formation of a well-mixed layer within the fog, induced by heat transfer from the soil and radiative effects, depending on the fog optical depth. This yields enhanced mixing and additional droplet activation well within the fog layer. UCLALES-SALSA also reproduces the removal of fog droplet by sedimentation. Sensitivity tests with varying aerosol concentration but with zero horizontal wind reveal the significant impact of the aerosol concentration e.g. on the growth of the fog layer depth. However, when realistic wind profiles (with shear present) are introduced, the dynamics of the mixing mask out most of the differences between model runs with different aerosol concentrations.

ACKNOWLEDGEMENTS

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REFERENCES


METHANE EMISSION ESTIMATES FOR NORTHERN HIGH LATITUDES BY CARBONTRACKER EUROPE-CH4

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Keywords: METHANE BUDGET, ATMOSPHERIC METHANE, ARCTIC, DATA ASSIMILATION.

INTRODUCTION

The atmospheric methane concentration in the early 21st century has two phases; a steady period before around 2007, and a period of increasing methane levels thereafter (Dlugokencky et al., 2009). The reasons for the increase have been discussed intensively in recent studies (Heiman, 2011), and the emissions from wetlands and peatlands in northern high latitudes (NHL, 50°N>) have been considered as one of the potential causes. The Arctic permafrost is estimated to contain 1672 PgC of organic carbon, which accounts for 50% of global belowground carbon pool (Tarnocai et al., 2009). As global warming exceeds, the permafrost thaw and extent of peatland and wetland will increase. Peatland and wetland are the most dominant biospheric source of methane today, accounting for 30% of total methane emissions (Kirschke et al., 2013). However, the estimates of methane emissions from northern boreal peatland and wetland have large uncertainty, mainly because available observations are limited to fully understand the biogenic processes, changes in ecosystems, and adoption of these to climate change.
In this study, we estimate the global methane emissions for 2004-2014 using CarbonTracker Europe-CH₄ (CTE-CH₄) data assimilation system, constrained by atmospheric methane mole fraction observations from various institutes and networks. Using an extensive network of observations in NHL, our focus is to estimate methane budgets in the northern boreal region.

METHODS

Global methane emissions were estimated by CTE-CH₄ data assimilation system, constrained by a set of observations that consists of 51 sites in NHL and 100 sites elsewhere globally. Since CTE-CH₄ is a global model, the sites outside NHL are important to constrain background atmospheric methane concentrations and emission budget globally.

For prior emissions, estimates from LPX-Bern dytop ecosystem model, and EDGAR v4.2 FT2010 inventory were used for biospheric and anthropogenic sources, respectively. Those emissions were optimized globally based on modified TransCom and land-ecosystem regions. For other sources, GFED v4.1(fire), Ito and Inatomi (2012) (termites), and Tsuruta et al. (2016) (ocean) are included, but not optimized.

The link between the prior emissions and the atmospheric concentrations are driven by the atmospheric chemistry transport model, TM5 (Krol et al., 2005). TM5 is constrained by ECMWF ERA-Interim meteorological fields, interpolated to 3 hourly fields. The horizontal resolution of TM5 is 1°×1° (latitude×longitude) over Europe, and 6°×4° globally.

CONCLUSIONS

Figure 1. Annual and monthly total LPX-Bern dytop (prior) and CTE-CH₄ (posterior) methane emission estimates for 50°N-90°N.

The estimated annual total emissions in the NHL showed an increasing trend during 2004-2007, but no indication of strong trend was found for 2008-2014. The emissions in the beginning of the period was highly dependent on number of observations, especially in Eurasian boreal region. Therefore, we assume the increase in this period is not realistic and the emission estimates were underestimated by the limited amount of observations available from NHL in the beginning of the period. The annual mean emission
estimates were 5-10 Tg CH₄ yr⁻¹ higher in the posterior, and most of the increase was seen in summer and autumn. High methane emissions from northern boreal region during summer and autumn is mainly due to biospheric sources, such as peatland and wetland. This indicates that the peatland and wetland emissions estimated by LPX-Bern dytop may be underestimated, rather than the anthropogenic emissions from EDGAR v4.2 FT2010 inventory. Although the effects of the NHL observations were significant in the emission estimates in NHL, these observations had little effect on the emission estimates elsewhere.

ACKNOWLEDGEMENTS

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REFERENCES

CAUSES OF EUROPEAN WEATHER FORECAST BUSTS

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Keywords: forecast bust, convection, initial conditions, OpenIFS

INTRODUCTION

Weather forecast models usually perform well but occasionally poor forecasts occur. These moments of poor performance are called forecast busts. A bust can be defined in many different ways but according to Rodwell et al. (2013) a bust occurs when the anomaly correlation coefficient of a day six forecast of the 500 hPa geopotential height over Europe drops below 40%.

Many of busts occurring in spring and early summer originate from convection over North America, mostly near the Great Lakes (Grazzini and Isaksen 2002). Data assimilation systems occasionally have trouble fitting modelled and observed fields together when extreme convection occurs. This may cause large analysis increments, with larger than normal risk of errors in initial conditions derived from the assimilated fields. Also, a bust can result from a sensitivity of a model to errors in initial conditions.

The purpose of this study is to determine the reasons why the forecast with a lead time of six days initiated on the 10th of April 2011 fails over Europe on the 16th of April. First we consider how the control forecast and ensemble members differ from reanalysis over Europe on day 6 of the forecast and then we consider errors in precipitation, convective available potential energy (CAPE), and Rossby wave source fields over the United States. Where there is precipitation, ascent and divergence occur in upper troposphere. Therefore, strong convection over the central US on the 10th of April can have an effect on the large scale dynamics. These effects are considered by analysing fields of Rossby wave source and potential vorticity.

METHODS

We use the Open Integrated Forecasting System (OpenIFS) cycle 38r1 weather model. IFS cycle 38r1 was the operational model at the European Centre for Medium Range Weather Forecasts (ECMWF) from the 19th of June 2012 to the 25th of June 2013. OpenIFS is a model version without data assimilation. Resolution of the model is spherical truncation T255, which corresponds to approximately 80 km grid spacing. We use also data from ECMWF Interim Reanalysis (ERA-Interim). ERA-Interim is based on IFS cycle 31r2 and it contains 4D variational data assimilation system with a 12 hour analysis window. The resolution of ERA-Interim is T255 with 60 vertical levels the uppermost being at 0.1 hPa. Temporal resolution is 6 hours in most of the data but 3 hours in precipitation.

At first we had to verify that the forecast bust occurs also in OpenIFS. We knew that the bust occurred at least in IFS of ECMWF and in several other weather models of different meteorological agencies (Rodwell et al. 2013). We ran 13 deterministic 10 day forecasts. The first one was initialised on the 1st of April 2011 and the last one on the 13th of April. Each forecast was initialised at 00 UTC. The verification of the forecast bust was done by calculating the anomaly correlation coefficient for the 500 hPa geopotential height over Europe at day 6 of the forecast. An anomaly correlation coefficient (ACC) is a quality measure of weather forecasts. It measures how similar the forecast field is to the corresponding analysed field (Inness and Dorling 2013). The anomaly correlation coefficient is

\[ ACC = \frac{\sum (F - C)(A - C)}{\sqrt{\sum (F - C)^2(A - C)^2}} \] (1)
where $\Sigma$ means a sum over grid points in a defined area, $F$ is forecast, $A$ reanalysis and $C$ is climatological value.

The ACC was used to find the initialisation day when the forecast gives the worst result 6 days later. The worst initialisation day is the 10\textsuperscript{th} of April. After verifying that the bust occurs in OpenIFS we further investigated the worst control forecast. This forecast performed the worst in terms of ACC. We also ran 5 ensemble members with slightly perturbed initial conditions in order to obtain a range of different outcomes. The initialisation date of the ensemble is the same as of the control forecast. To shed some light on the reasons behind the forecast bust we first took a look what happened over Europe. Next we looked at errors in CAPE, precipitation and Rossby wave source fields. Rossby wave source contains the forcing terms of the vorticity equation (Sardesmukh and Hoskins 1988).

\[ S = -v_x \cdot \nabla \xi - \xi D. \]  

where $v_x$ is divergent wind vector, $\xi$ is absolute vorticity and $D$ is divergence.

RESULTS

Both in the forecast and reanalysis there is a strong southerly, very warm and humid airflow at the surface in the Central US before and at the time of strong convection. The surface airmass is moving underneath a rather cool, mid to high level airmass. This leads to steep lapse rates and a build-up of CAPE. In this case this development of instability in OpenIFS seems to be sensitive to errors in initial conditions. There is a significant displacement error and a slight magnitude error in CAPE already in the 6-hour forecast, as OpenIFS forecasts the area of large CAPE to be too far north-east and it also underestimates the magnitude (figure 1).

![Figure 1. CAPE and error of CAPE 10th Apr 06.00 UTC](image-url)

The error in CAPE has an effect on the mesoscale convective system (MCS), which formed near the Kansas-Nebraska border on the 9\textsuperscript{th} of April at 21 UTC. Twelve hours into the forecast, at 12 UTC on the 10\textsuperscript{th} April, the eastward propagating MCS is moving too fast and is on a too southerly track in the OpenIFS forecast.
Precipitation in wrong place causes upper level divergence in a wrong place. The erroneous divergence modifies Rossby waves through the vorticity equation and Rossby waves transport the error from North America to Europe. There are errors in Rossby wave source over eastern North America (figure 3). The positive values of RWS are slightly too large over Eastern Canada so the RWS is strengthening the ridge too much. On the 16th of April OpenIFS has trouble in forecasting whether the weather regime will change or not. The control forecast and the five ensemble members all predict blocking over Europe but there is no sign of blocking in reanalysis (figure 4).
Figure 3. The Rossby wave source (shaded) and 500 hPa geopotential height (contoured). Upper part is the control forecast and lower part is the reanalysis. RWS is the forcing term of the vorticity equation so positive values mean that the RWS is building ridges higher and negative values mean that the RWS is digging troughs deeper.

Figure 4. 5400 metre geopotential height six days after the initialisation of the forecasts. Green contour is the control forecast and black contour is ERA-Interim reanalysis. Other contours are different members of the ensemble. All forecasts showed that the weather regime will change from relatively westerly flow to a blocking high pressure system over northern Europe. Reanalysis data, however, did not show the change in the weather regime. Probably even small errors in initial conditions were enough to trigger the change in the forecasts.
CONCLUSIONS

The results of this study show how the OpenIFS weather model occasionally reacts strongly to errors in initial conditions. The studied errors in precipitation over North America seem to lead to errors in the source and subsequent propagation of Rossby waves, which eventually lead to errors in the large-scale circulation patterns over Europe 6 days later. This agrees well with previous studies (Grazzini and Isaksen 2002). The OpenIFS forecast shows a change in the weather regime but this transition was not found in the reanalysis. In the reanalysis, westerly flow prevailed.

Forecasting change in weather regime is occasionally difficult for weather models. Usually models tend to underestimate blocking or miss it completely so it is interesting, that in this case the opposite happens. It seems that possible reason for this forecast bust is coincidence of errors in initial conditions and high error sensitivity of models.

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REFERENCES


RE-EVALUATING THE CONTRIBUTION OF SULFURIC ACID IN ATMOSPHERIC NANOPARTICLE GROWTH

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Keywords: NEW PARTICLE FORMATION, SULPHURIC ACID, ORGANIC COMPOUNDS, ACSM.

INTRODUCTION

In atmospheric new particle formation the survival probability of a newly-formed 1-2 nm particle depends strongly on its growth rate and subsequently on the concentration of condensable vapours in the air. However, atmospheric chemistry responsible for the growth of newly-formed aerosol particles to climate-relevant sizes is still not very well known. We utilized one year of simultaneous measurements of aerosol particle size distributions and on-line PM1 chemical composition at the Welgegund measurement station in South Africa to investigate the composition of the growth in regional scale new particle formation (NPF) events.

METHODS

Measurements were carried out at the Welgegund measurement station, 26.57°S, 26.94°E, 1480 m a.s.l., from 1 September 2010 to 30 August 2011. Welgegund is located on a private farm in grazed savannah grassland environment with no local anthropogenic sources. Aerosol particle size distribution was measured with a differential mobility particle sizer (DMPS) (Petäjä et al., 2013) and air ion size distribution with an air ion spectrometer (AIS) (Mirme et al., 2007). On-line PM1 chemical composition was measured with an aerosol chemical speciation monitor (ACSM) (Ng et al., 2011; Tiitta et al., 2014). Auxiliary measurements included among others Sulphur dioxide and global radiation (Petäjä et al., 2013). The growth rate in NPF events was analysed from DMPS and AIS measurements according to the guidelines presented by Kulmala et al. (2012); a detailed description on connecting the size distribution and chemical composition measurements is given by Vakkari et al. (2015).

RESULTS

During the measurement period from September 2010 to August 2011 we could estimate the chemical composition of the growth for 88 NPF events. Not surprisingly, the growth was dominated by either sulphuric acid (H₂SO₄) accompanied by ammonium or organic compounds depending on the air mass origin and size of the growing particles. The contribution of H₂SO₄ was larger during the early phases of the growth, but in clean conditions organic compounds originating from either biogenic emissions or savannah fires dominated the growth from 1.5 nm up to climatically relevant sizes (Vakkari et al., 2015).
We compared the observed growth by H$_2$SO$_4$ to the calculated growth by H$_2$SO$_4$ from gas phase H$_2$SO$_4$ concentration, which is a commonly-used method if no aerosol chemical composition measurements are available. In clean conditions these two methods agreed reasonably well, but in high H$_2$SO$_4$ concentrations the gas phase H$_2$SO$_4$ calculation underestimated the observed growth by H$_2$SO$_4$ by up to a factor of ten (Vakkari et al., 2015). We attribute the discrepancy mostly to the uncertainty in gas phase H$_2$SO$_4$ measurements: at high concentration levels the clustering of H$_2$SO$_4$ molecules makes it more difficult to detect sulfuric acid with commonly-used mass spectrometric methods (Petäjä et al., 2011; Neitola et al., 2015), while there is little or no effect on the net flux of H$_2$SO$_4$ to the growing new particles.

CONCLUSIONS

In this study we have demonstrated that combining simultaneous measurements of aerosol chemical and physical properties can be utilised to infer the contributions of different chemical species to the growth of freshly nucleated particles to climatically relevant sizes in the atmosphere. In clean conditions organic compounds dominated the growth from 1.5 nm up to climatically relevant sizes, whereas in sulphur rich atmosphere sulphate was found to dominate the growth. Comparison of the observed growth by H$_2$SO$_4$ to the calculated growth by H$_2$SO$_4$ from gas phase H$_2$SO$_4$ concentration showed that in clean conditions these two methods agreed reasonably well, but in high H$_2$SO$_4$ concentrations the gas phase H$_2$SO$_4$ calculation underestimated the observed growth by H$_2$SO$_4$ by up to a factor of ten.

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REFERENCES


INTRODUCTION

It has been suggested that the discrepancy between global models and measurements could best be reduced through the study of natural aerosols in environments with negligible anthropogenic influence. Antarctica is such an environment, anthropogenic emissions are smaller there than on any other continent. Antarctica is also a negligible contributor to global greenhouse gas (GHG) emissions, due to the cold and dry climate with year-round snow cover. However, open seas surrounding Antarctica are actively exchanging CO₂ with the atmosphere due to ocean circulation and biological activity of the marine organisms.

The primary goal of the four-year (2013 – 2016) project Atmospheric Composition and Processes relevant to climate change in ANTarctica (ACPANT), funded by the Academy of Finland, was to provide new scientific insight into atmospheric composition and associated processes relevant to climate change in the Antarctic atmosphere. The project was a consortium of the University of Helsinki and the Finnish Meteorological institute. ACPANT consisted of four thematic issues: i) atmospheric new-particle formation, ii) properties and sources of cloud condensation nuclei, iii) aerosol optical properties and iv) oceans and coastal shelf areas around Antarctica as sources and sinks of carbon dioxide and methane.

METHODS

The work was based on continuous measurements at three research stations located in Antarctica: the joint Italian-French Concordia station at Dome C in the upper plateau of East Antarctica, the German station Neumayer in coastal Antarctica, and the Argentinian station in Marambio – a small island at the northern tip of the Antarctic Peninsula. The continuous measurements were supported by intensive field campaigns at Neumayer and at the Finnish station Aboa, both in Queen Maud Land. Particle size distributions,
optical properties, and chemical composition of aerosols well as greenhouse gas concentrations were measured.

Recent results of the work conducted by the consortium at the various measurement sites have been presented, e.g., by Järvinen et al. (2013), Kyrö et al. (2013) and Teinilä et al. (2014. In this presentation selected results from all sites will be shown.

Figure 1. Locations of the sites where measurements during ACPANT were conducted.

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REFERENCES


HUMIDITY AND TEMPERATURE STRUCTURES ASSOCIATED WITH DEEP CONVECTION

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Keywords: Atmospheric deep convection, humidity

INTRODUCTION

Atmospheric deep convection is the key mechanism causing thunderstorms, tornadoes, and tropical cyclones. Over 2/3 of precipitation that reaches the surface of Earth occurs in the Tropics (Hong et al. 1999) where precipitation is mostly associated with deep convection. In summer, precipitation in midlatitudes is also typically associated with deep convective processes.

A recent study suggests that a large part of the spread of 1.5 – 5°C in the climate sensitivity in climate models can be traced back to atmospheric convective mixing between the lower and middle tropical troposphere (Sherwood et al. 2014). It is clear that in order to understand the climate sensitivity of our atmosphere, we must understand the physics of convection.

Deep convection is caused by the unstable stratification of mass in the atmosphere. In this basic mechanism for convection, humidity above the planetary boundary layer (PBL) has no role. Still, many studies show that deep convection is very sensitive to humidity above the PBL (e.g., Breherton et al. 2004, Sobel et al. 2004 and Holloway and Neelin 2009) with higher lower tropospheric humidity favoring subsequent convection. Humidity’s effect via entrainment on the formation of deep clouds and on downdrafts that bring cold air to the PBL have been suggested as reasons for the sensitivity of convection to humidity above the PBL. But the issue is not settled yet.

What is the mechanism increasing humidity above the PBL? Recent research has promoted the idea that it is the moistening effect of cumulus congestus clouds whose tops extend only to the midtroposphere. However, Hohenegger and Stevens (2013) show that the moistening by congestus clouds occurs too slowly to have an effect on the deep convection.

Based on the second author’s earlier study (Bister 1996), we suggest a mechanism for the increase of the moisture that depends on previous convection affecting the humidity and temperature of the same air mass. This mechanism may also help us understand why convection is so sensitive to humidity in the lower part of the free troposphere. To learn more about the tropospheric humidity and temperature structures associated with deep convection, we have first analysed soundings over the tropical oceans, where deep convection frequently occurs.

METHODS

To study how precipitation is related to the humidity and temperature structure of the troposphere, sounding data obtained from the Integrated Global Radiosonde Archive (IGRA) and precipitation data from the Tropical Rainfall Measuring Mission (TRMM) are analysed. We have analysed soundings from four stations that are located over the eastern Indian Ocean and the western Pacific warm pool. For each station, the soundings were divided into groups based on the amount of area-averaged precipitation from a time period of roughly 24 hours before the sounding. Area-averaged precipitation rates were calculated by taking the mean over an area of 5° in radius so that the station was in the middle. Six groups were formed so that one contained soundings where the amount of area-averaged precipitation was less than 0.5 mm during 24 hours before the sounding observation (PR0). The amount of area-averaged 24-hour accumulated precipitation in the other groups was 0.5-1 mm (PR1), 1-2 mm (PR2), 2-5 mm (PR3), 5-10
mm (PR4) and over 10 mm (PR5). For each group and for each station, the average vertical profile of relative humidity (RH) and temperature were calculated. Anomalies of RH and temperature were calculated by subtracting the average vertical profile of the non-precipitating group (PR0) from a precipitating group (PR1-PR5).

CONCLUSIONS

Figure 1 shows average vertical profiles of RH (a), RH anomaly (b) and temperature anomaly (c) in each group in Agana (13.48°N, 144.80°E). Figure 1b suggests that precipitation is associated with a positive RH anomaly throughout the troposphere and that the anomalies are largest in the 300-750 hPa layer.

![Figure 1](image)

Figure 1. Average vertical profiles of a) RH (%), b) anomalous RH (%) and c) anomalous temperature (°C) in the different groups in Agana. PR0 (black) is the average of radiosonde observations after the amount of precipitation during the previous 24 hours was less than 0.5 mm, PR1 (dark blue) 0.5-1 mm, PR2 (light blue) 1-2 mm, PR3 (purple) 2-5 mm, PR4 (red) 5-10 mm and PR5 (green) more than 10 mm.

The results from Agana show interestingly that precipitation is associated with a complex vertical temperature anomaly structure (figure 1c), which yields information about different processes occurring in mesoscale convective systems. Figure 1c shows a positive temperature anomaly in the 300-500 hPa layer,
most likely due to diabatic heating due to condensation in the anvil cloud associated with deep convection. The 500-750 hPa layer is characterized by a negative temperature anomaly, most likely due to diabatic cooling associated with evaporation of stratiform precipitation falling from the anvil cloud. Between 750-950 hPa, a positive temperature anomaly is seen, which is hypothesized to be due to adiabatic warming in evaporatively driven mesoscale unsaturated downdrafts. The layer below 950 hPa is characterized by a strong negative temperature anomaly, likely due to convective-scale saturated downdrafts driven by the evaporation of intense deep convective precipitation. Figures 1b and 1c show that the anomalies of RH and temperature are larger with higher amounts of precipitation at almost all altitudes. Similar temperature structures, with a relatively warm layer between 750-950 hPa were observed also over the other stations (not shown).

We have studied the sensitivity of the observed temperature structures to changes in local sea surface temperature, mean 200-750 hPa tropospheric temperature and the effect of convectively coupled Kelvin waves and the Madden-Julian oscillation. According to our results, the above mentioned factors did not affect the existence of the temperature anomalies seen in figure 1c, although they did have an effect on the magnitude of the anomalies (not shown).

This work continues in analysing the causes and effects of the observed humidity and temperature structures using both data analysis and numerical modelling.

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REFERENCES


AUTOMATIC RECOGNITION OF NEW PARTICLE FORMATION EVENTS

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Keywords: NEW PARTICLE FORMATION, MACHINE LEARNING, STATISTICS.

INTRODUCTION

Reliable recognition of occurrence of new particle formation is of utmost importance for gaining insight into the process. Traditionally this has involved expert opinions of one or more scientists, based on manual inspection of particle number—size distribution from a DMPS instrument. The data are presented as images, and the “shape of a banana” is often more or less clearly discernible, inspiring the thought of automatizing the process with readily available tools of machine learning and computer vision.

METHODS

Particle number—size distribution has been actively measured by DMPS instruments in Hyytiälä, Finland, for two decades. The data has been evaluated and labelled daily according to the principles presented in Dal Maso et al. (2005), which constitutes a sizeable training set for machine learning algorithms.

The data from each day was normalized and concatenated into a long vector, and then combined into a large matrix. While being simple, this approach does have the disadvantage that the number of features becomes roughly equal to the number of training samples. Nevertheless, the data was used to train and test many classification algorithms in the Scikit-Learn software (Pedregosa et al., 2011). The so-called “undefined” days were left out due to their ambiguity. The tested algorithms included linear discriminant analysis (LDA), logistic regression, 9-nearest-neighbor classifier, support vector machine and AdaBoost.

The distinction between different classes is not always clear even for the human expert, however. For this reason, the data were further reduced into “sure” cases of new particle formation or not. Although the binary classifier is trained only with rather sure data, a probability interpretation may be used to gain insight into the less obvious cases. This arises naturally with the logistic regression classifier, which allows for direct probability interpretation.

RESULTS AND DISCUSSION

Using new particle formation event types Ia, Ib, II, “negative” and “bad data” as labels for the data, several machine learning algorithms from the Scikit-Learn software were trained. They typically reached a mean accuracy of around 70-80% with the exception of LDA, whose accuracy varied greatly and was often below 60%. Figure 1 presents a transform of data by the LDA classifier on axes that maximize class separation, which shows the difficulty that it has with the different positive classes. The lower accuracy of LDA is unsurprising, as the algorithm assumes that the different classes share a covariance matrix, which is untrue for this kind of data; nevertheless, it is an illustrative example.
The inclusion of only the sure cases increased the accuracy of the logistic regression classifier to around 96%, which is now to say only whether a new particle formation event occurred or not. The probability interpretation of this classifier allows for closer inspection of the wrongly classified days, and reveals that in many cases the probability was close to 50%, see Figure 2. This calls for further improvement in the algorithm.

Figure 1. The results of linear discriminant analysis classification transformed on component axes. The classes are: 1 = "Ia", 2 = "Ib", 3 = II, 8 = "non-event", 10 = "bad data". Note the considerable overlap in “positive” cases.

Figure 2. Example of new particle formation event undetected by logistic regression, although by very slight margin: the algorithm states probabilities 0.498 and 0.502 for event and non-event, respectively.
CONCLUSIONS

Experiments with machine learning algorithms have been carried out with the goal of reliably automatizing new particle formation event classification. At the moment logistic regression is able to determine the occurrence of new particle formation with very high accuracy, but it still requires some improvement and consistency before deploying into production.

ACKNOWLEDGEMENTS

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REFERENCES

HYGROSCOPICITY OF SUB-25 NM DMA-H₂SO₄ PARTICLES – COMPARISON BETWEEN MEASUREMENTS AND MODEL PREDICTIONS

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Keywords: HYGROSCOPICITY, DIMETHYLAMINIUMSULFATE.

INTRODUCTION

Aerosol hygroscopicity is an important property determining the aerosol particles’ ability to take up water under humidified conditions. In the case of cloud formation, aerosol hygroscopicity is therefore a fundamental factor determining which particles can activate into cloud droplets (Väisänen et al., 2016). On the other hand, water uptake also creates a pathway for aqueous phase processes, which can further alter aerosol properties and composition via changes in gas-particle phase partitioning (McNeill, 2015).

Dimethylaminium and sulfate ions have been found in the particle phase during the growth of freshly nucleated aerosol particles (e.g., Smith et al., 2010). Therefore, knowledge about the hygroscopicity of dimethylaminiumsulfate (DMAS) particles is required to simulate the growth of DMAS containing nanoparticles. However, the current thermodynamic models used for this purpose are typically tested against large particles or bulk systems (e.g., Clegg et al., 2013) rather than particle sizes relevant to newly formed aerosol population.

In this work, the aim is to test the performance of a state-of-art bulk thermodynamic model (E-AIM) in capturing the sub-saturated hygroscopicity of DMAS particles in the size range of 10 to 25 nm.

METHODS

Water solutions with different molar ratios of dimethylamine (DMA) and sulfuric acid (SA) were prepared to generate polydisperse DMAS particles with a conventional aerosol atomizer (Topas ATM 226). A total of five different solutions were made with nominal (molar) DMA-SA ratios (DMA:SA) of 2:1, 3:2, 1:1, 1:2 and 1:3, and each of these solutions had an approximate concentration of 3 wt %. In order to reduce the uncertainties in experimental results (e.g., due to DMA evaporation), the chemical composition of the polydisperse aerosol population was measured with an Aerodyne HR-ToF-AMS.

The hygroscopic growth of 10, 15, 20 and 25 nm particles was measured with a custom made hygroscopic tandem differential mobility analyzer (nano-HTDMA). Briefly, nano-HTDMA consists of two differential mobility analyzers and a humidifier. The first mobility analyzer (TSI 3085) selects the dry size of interest ($D_{dry}$), and the second mobility analyzer coupled with a condensation particle counter (TSI water-based CPC 3785) measures the wet particle size ($D_{wet}$) after the dry monodisperse aerosol population has been exposed to certain relative humidity (RH).

The measured hygroscopic growth factors ($GF = D_{wet}/D_{dry}$) were compared to model calculations performed with E-AIM (Clegg et al., 1998). Principally, E-AIM is a bulk thermodynamic equilibrium model of gaseous and particulate phases with a built-in acid-base chemistry. Since E-AIM only accounts the bulk chemical system with a flat surface, Kelvin correction was applied to the model results.
RESULTS AND CONCLUSIONS

Table 1 summarizes the nominal strengths of the prepared DMA-SA solutions and the respective molar ratios derived from AMS measurements. While the values seem to agree at DMA:SA = 2:1 and 3:2, the more acidic solutions were conversely accompanied with elevated fractions of DMA. This could indicate that the particle composition may have changed during the sampling process for example due to dilution or drying. However, the exact reason behind the observed trend is yet to be confirmed.

<table>
<thead>
<tr>
<th>Nominal strength (mol:mol)</th>
<th>Measured composition (mol:mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>1.95:1</td>
</tr>
<tr>
<td>3:2</td>
<td>2.7:2</td>
</tr>
<tr>
<td>1:1</td>
<td>1.7:1</td>
</tr>
<tr>
<td>1:2</td>
<td>1:1</td>
</tr>
<tr>
<td>1:3</td>
<td>2.4:3</td>
</tr>
</tbody>
</table>

Table 1. Comparison between the nominal and measured DMA-SA ratios.

Figure 1 shows a comparison between the measured and modelled hygroscopic growth factors. Here, the measurement data are plotted against the AMS derived molar fractions. Therefore, since the AMS was constantly sampling the polydisperse aerosol with vacuum aerodynamic mode diameter around 300 nm, one needs to assume that the particle composition does not depend on particle size. According to our observations, all the modelled GFs appear lower than those measured with nano-HTDMA. Furthermore, the discrepancy between the model and the measurements does not seem to exhibit a clear composition dependence.

Several possible explanations exist for the observed discrepancy between the measured and modelled GFs. The first possible source of error arises from the composition measurements. As it was addressed in the previous paragraph, the particles measured with an AMS were much larger than those sampled with nano-HTDMA. Furthermore, it is possible that the particle composition has further changed inside the nano-HTDMA due strong dilution of the surrounding gas phase. Secondly, the differences may also arise from the uncertainties in the applied DMA-SA-H\(_2\)O thermodynamics, as well as from the applicability of the
model for concentrated solution droplets. Assessing the relative importance and relevance of different sources of uncertainty is a topic of an ongoing research.

ACKNOWLEDGEMENTS

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

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

INTRODUCTION

The CLOUD chamber facility (Kirkby \textit{et al.} 2011; Duplissy \textit{et al.} 2016) located at CERN enables the study of the effect of different levels of ionizing radiation on new particle formation. It is equipped with a high voltage field cage (clearing field) which can be used to remove all ions from the chamber. One of the key features of the CLOUD experiment is the extremely low level of contaminants, which allows the investigation of new particle formation in different chemical regimes under precisely defined conditions. While ion concentrations have been found to affect nucleation rates in previous studies (Almeida \textit{et al.} 2013, Kirkby \textit{et al.} 2016) the size resolved charge fractions were not yet subject to a detailed study.

METHODS

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

Besides particle counters and ion spectrometer (NAIS) a set of mass spectrometers and sensitive gas monitors were measuring the chemical composition of formed clusters and their precursors. The studied regimes include a mixture of monoterpenses (alpha pinene, delta-3-carene; 150–1200 pptv), sulfuric acid ($<1e5–5e7 \text{ cm}^{-3}$), nitrogen oxides (0–5 ppbv) as well as ammonia (0–3 ppbv). With this broad set of experiments we aim to shed light on the significance of ion induced nucleation processes in different environments.

RESULTS

We observed that particles are likely to be charged when they are very small (1.2 nm in diameter) and when conditions for nucleation are not favorable (e.g. low precursor gas concentrations). In these situations, the charge is necessary to stabilize the cluster, and ions are important for new particles to form.
However, as the particles grow to slightly larger sizes (1.7 nm), many become more stable and get neutralized by recombination. When reaching a diameter of 2.2 nm, almost all of the particles are neutral. In our experiments we studied five chemical environments, from pure biogenic vapors to conditions similar to Hyytiälä, Finland, studying the effects of monoterpenes, sulfuric acid, nitrogen oxides, and ammonia.

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

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REFERENCES

INCREASED FRACTION OF AEROSOL INORGANIC COMPONENTS CONTRIBUTES TO VISIBILITY DEGRADATION

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Keywords: aerosol, visibility degradation, satellite data, inorganic precursors

INTRODUCTION

The formation mechanism of increased haze events during the last decades in China is still not very clear, although climate factor may be important\(^1,2\). Here, we found an interesting phenomenon that the surface visibility decreased much in high relative humidity (80\%-90\%) than that in dry conditions (relative humidity <40\%) from 1980 to 2010 in most regions of China. For this phenomenon, we hypothesis that an increasing fraction of inorganic components in aerosol particle may be responsible.

Higher mass fractions of inorganic may lead to increased aerosol water up take and light scattering ability of aerosol with elevated relative humidity. Satellite observation of aerosol precursors of NO\(_2\), SO\(_2\) and the fraction of fine mode aerosol showed an increasing trend significantly. Some in-situ measurement of aerosol chemical composition and GEOS-Chem model confirmed the increased trend of inorganic components in PM\(_{2.5}\), which can verify our hypothesis. Our study demonstrates that increased fraction of inorganic components in aerosol particle is a critical factor of the frequently occurred haze days during the latest 30 years and the reduction of nitrate, sulfate and their precursor gases would be efficient for better air quality in China.

METHODS

The daily averaged visibility and relative humidity data in 262 sites of China are obtained from the Integrated Surface Dataset (ISD) from National Oceanic and Atmospheric Administration National Climate Data Center of the USA. The visibility observations were made three times a day at 8-hour intervals begins at 00:00 by well trained technicians. They measured visual range using distinctive markers, such as tall buildings, mountains and towers, to which the distance from the meteorological monitoring stations are known.

The column amount of NO\(_2\), SO\(_2\) and CH\(_2\)O data are obtained from SCIAMACHY (Scanning Imaging Absorption spectrometer for Atmospheric CHartographY).

The aerosol optical depth, fine mode aerosol optical depth fraction and aerosol Ångstrom exponent (SÅE) are obtained from MODIS.
CONCLUSIONS

Figure 1 A schematic picture shows the process of enhanced aerosol inorganic components leading to increased aerosol water uptake ability and relative visibility degradation. The plus and minus symbols represent the strengthen or weaken of the specific process.

ACKNOWLEDGEMENT

We thank NOAA, SCIAMACHY and MODIS team for providing high quality data.

REFERENCES


IMPLEMENTATION OF A NEW SIZE-SEGREGATED AEROSOL NUMBER EMISSIONS MODULE IN GLOBAL CLIMATE MODELING

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Keywords: AEROSOL, NUMBER SIZE DISTRIBUTION, GLOBAL CLIMATE, ECHAM.

INTRODUCTION

Climate models are important tools that are used for generating climate change projections, in which aerosol-climate interactions are one of the main sources of uncertainties. The number of particles emitted from anthropogenic sources in the atmosphere is an important parameter used in these models for assessing aerosol-cloud interactions. However, the input anthropogenic aerosol number emissions are usually converted from mass, taken e.g. from the Aerosol Comparison (AeroCom) inventory, to number size distribution through a very simplistic method depending uniquely on chemical composition, particle size and density, which are defined for a few very wide main source sectors. In this work, the anthropogenic particle number emissions converted from the Aerosol Inter Comparison data set (AeroCom) mass in the ECHAM-HAM climate model are replaced with the recently formulated number emissions from the Greenhouse Gas and Air Pollution Interactions and Synergies (GAINS)-model, where the emission number size distributions vary e.g. with respect to fuel and technology. We focus our analysis on accumulation mode particles (Dp > 100 nanometers) because of (i) their capability of acting as cloud condensation nuclei (CCN), thus forming cloud droplets and affecting Earth's radiation budget, and (ii) their dominant role in forming the coagulation sink and thus limiting the concentration of sub-100 nanometers particles. In addition, the estimates of anthropogenic CCN formation, and thus the forcing from aerosol-climate interactions are expected to be affected. Analysis of global particle number concentrations and size distributions reveal that GAINS implementation increases the global CCN with regional factors up to 10. Comparison between modeled and observed concentrations shows that the increase in number concentration for accumulation mode particle agrees well with measurements, but it leads to a consistent underestimation of the nucleation and Aitken mode (Dp < 100 nm for both) particle concentrations. This suggests a revision of the currently applied model's nucleation and growth schemes.

METHODS

a. The new emissions from GAINS model are extracted and implemented in the ECHAM-HAM model to update its current version of emission sectors.

b. Once the new emission modules are implemented, a sensitivity evaluation of the simulated aerosol concentrations are performed to evaluate aerosol concentration behaviour in case either mass or number-based emissions will be used.

c. An analysis of particle number size distribution and concentration including a temporal assessment are performed, first for measurement sites in Finland and Scandinavia, and later for sites in Europe and on other continents. In this step the shares of anthropogenic and biogenic/atmospheric aerosol formation in both modelled and measured size distributions are estimated. Moreover, a comparison between model outputs and observational data are performed to evaluate the accuracy of the models projections.
d. ECHAM-HAM model with updated emission sectors are used to evaluate the impact of current aerosol emissions, technology upgrades and emission policies on climate. This investigation takes into account the contribution of anthropogenic aerosol formation and anthropogenic sources.

![CCN at S=0.200 % - Annual](image)

Figure 1. GAINS/AEROCOM annual ratio of CCN at 0.2% supersaturation.

**RESULTS**

- In comparison to AeroCom, GAINS emissions produced much higher CCN concentrations, in agreement with the measurements.
- The underestimation of smaller particles concentration highlighted the sensitivity of chosen nucleation scheme to other aerosol parameters in the model, suggesting further revision of both GAINS emissions factors (Paasonen et al., 2016) and nucleation module in the ECHAM.
- More observations within the PEEX domain are urgently needed in order to better evaluate the model results.
- The implementation of up-to-date secondary organic aerosols (ELVOCS) and the development of a standalone black carbon module shall represent the continuation of this work to improve the chemistry module in the ECHAM.

**REFERENCES**


SOURCE CHARACTERIZATION OF HIGHLY OXIDIZED MULTIFUNCTIONAL COMPOUNDS IN A BOREAL FOREST ENVIRONMENT USING POSITIVE MATRIX FACTORIZATION

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Keywords: HOMs, PMF, CI-APi-TOF.

INTRODUCTION

Large amounts of volatile organic compounds (VOCs) are emitted into the atmosphere from both biogenic and anthropogenic sources (Atkinson and Arey, 2003). These VOCs are oxidized in the atmosphere, which leads to thousands of structurally distinct products, containing many functionalities (Hallquist et al., 2009). A subset of these products become highly oxidized multifunctional compounds (HOMs, Ehn et al., 2012), and although generally considered a minor pathway in VOC oxidation, they play a crucial role in atmospheric aerosol formation (e.g. Kulmala et al., 2013; Ehn et al., 2014), and thereby both air quality and climate.

As HOMs are important compounds linking VOCs to SOA, quantitative simulation of SOA formation requires detailed understanding of HOM formation. Recently laboratory studies have suggested that the formation of HOMs consists of two consecutive processes: 1) VOC oxidation forming peroxy radicals (RO₂) able to auto-oxidize through intramolecular H-abstraction, leading to multiple O₂ additions; and 2) termination reactions, which terminate the auto-oxidation by converting RO₂ radicals into closed-shell molecules (Ehn et al., 2012, 2014; Jokinen et al., 2014, 2015; Boyd et al., 2015). The large variety of oxidants and terminators leads to critical branching steps in the atmospheric oxidative pathways, eventually resulting in a large number of different HOM molecules. With the recently developed instrument named chemical ionization atmospheric pressure interface time of flight mass spectrometry (CI-APi-TOF) (Junnilen et al., 2010, Jokinen et al., 2012), we are able to sensitively and selectively detect HOMs with high oxygen-to-carbon ratio. However, the detailed formation pathways of these observed compounds remain poorly understood. One of the fundamental reasons is the lack of robust methods to analyze the complicated ambient data (e.g. mass spectra containing >>100 molecular ions) and to link ambient observations and chamber studies.
Positive matrix factorization (PMF) (Paatero and Tapper, 1994) allows for time resolved mass spectra to be expressed as a linear combination of a finite number of factors, assuming that the factor profiles are constant and unique (Ulbrich et al., 2009). Since this method does not require a-priori information about the factors, it is an ideal technique for extracting information from ambient measurements where the detailed chemistry, sources, and atmospheric processes are complex. PMF analysis has been widely used on aerosol mass spectra (e.g. Zhang et al., 2011 and the references therein), and also on proton transfer reaction mass spectrometer (PTR-MS) data.

In this work, we report the first success of utilizing PMF on CI-APi-TOF data. We examine the degree to which the PMF factors represent the dominant HOM formation pathways at the observation site, and attempt to validate the retrieved factors by comparison to existing chamber data and correlation with other co-located measurements. Our results link the ambient measurement to previous chamber studies, and identify needs for future research efforts in this area. This work also provides new perspectives on using PMF to understand the variation of short-lived species, e.g. HOMs.

**METHODS**

In this study, the measurement data was obtained from SMEAR II located in Hyytiälä, Southern Finland in spring 2012. The station is surrounded by boreal conifer forest and is described as a rural continental background measurement site. There are also occasionally polluted air masses reaching the site causing high aerosol loadings and high concentrations of gas-phase pollutants. Ambient meteorological conditions such as temperature, relative humidity (RH), solar radiation, wind speed and direction, particle concentration and size distribution, as well as concentrations of aerosol particles and several trace gases, e.g. carbon dioxide (CO$_2$), carbon monoxide (CO), sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$) and ozone (O$_3$), are continuously monitored at the station.

The estimation of measurement uncertainty (error matrix) is critical in PMF and since there was no previous research on applying PMF to CI-APi-TOF data, we derived the equation of error matrix for this new data set based on laboratory experiments, which showed good agreement with the equation used in aerosol mass spectrometer (AMS). The free parameters in the equation seem to be independent of temperature, instrument tuning, and detected chemical species.

The PMF solutions are firstly evaluated based on the mathematical diagnostics, including the Q value, Q distribution, and the fraction of explained variation by the model. Further verification of PMF results relies on the interpretability, which usually needs many considerations including: 1) a direct comparison of the retrieved factors to reported reference mass spectra; 2) key molecules as the fingerprint of a specific source; 3) The temporal correlation between the factors and related trace gases; 4) the repetitive temporal or diurnal variation patterns that indicate specific human activities or meteorological patterns; and 5) information regarding to air masses such as wind direction analysis or air mass trajectories.

**CONCLUSIONS**

The HOM data is optimally explained by six factors, which have distinct profiles and diurnal patterns, as shown in Fig.1 and Fig.2 respectively. The two nighttime factors likely represent the oxidation of monoterpene initiated by O$_3$ and NO$_3$, respectively. The profile of the O$_3$+ monoterpene factor is similar to the reference spectrum in previous chamber studies where only O$_3$ and monoterpenes were injected (Ehn et al., 2014), and the uncentred correlation coefficient between the factor and the reference spectrum is 0.91. The NO$_3$ + monoterpene reaction channel is supported by the detection of nitrogen-containing dimer compounds. In the early morning, both nighttime chemistry channels are suppressed by NO reaction, shown by the appearance of factors representing RO$_2$ + NO reactions. The major peaks in the first daytime factor are C$_{10}$H$_6$O$_5$·NO$_3$, whose parent RO$_2$ radicals are likely from O$_3$ + monoterpene. Two other daytime factors are retrieved, though the underlying chemical processes forming those components are not clearly understood. One daytime factor correlated well with sulfuric acid, suggesting the chemistry represented by this factor could be controlled by the OH radical. The third daytime factor contained many smaller HOM
molecules and showed notable correlation with UVB and temperature. The interpretation is that the formation of these smaller HOM molecules are OH-initiated, and their gas-phase concentration is affected by temperature probably through particle-gas partitioning. Apart from these five “local” factors, the sixth factor is interpreted as a transport factor, due to its similar temporal variation to SO$_2$ and its prominent peak C$_6$H$_5$NO$_3$, a reported tracer of biomass burning.

Among the six factors retrieved by PMF, only the nighttime type-1 factor (O$_3$ + monoterpene) has been confirmed in the laboratory. However, the retrieval of this factor also strongly supports the validity of the model results. The deduced chemical processes for the nighttime type-2 factor (NO$_3$ + monoterpene) and the daytime type-1 factor (RO$_2$ + NO) are supported by their correlations with other co-located measurements. To confirm and better understand these two factors, laboratory experiments are needed to investigate the yields and dependence on other parameters. The daytime factors are harder to interpret. However, testing the hypotheses suggested by PMF solutions will be a good starting point for future studies.

In summary, running PMF on CI-API-TOF data was successful, and the results presented in this paper improve our understanding of HOM production by confirming current knowledge and inspiring future research directions.

ACKNOWLEDGEMENTS

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Figure 1. Factor profiles in 6-factor PMF. The total signal of each factor is normalized to unity, and y-axis is the fraction of variables in the factor in percentage.

Figure 2. The diurnal cycle of PMF factors, selected meteorological parameters, and trace gas concentration.
EVAPORATION OF α-PINENE DERIVED SOA PARTICLES UNDER DRY AND HUMID CONDITIONS


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Keywords: SOA, VISCOSITY, VOLATILITY, VBS.

INTRODUCTION

Secondary organic aerosol (SOA) is formed in the atmosphere through chemical reactions from volatile precursor gases. Atmospheric SOA is a complex system that comprises numerous compounds, and many properties of SOA are still poorly known. SOA constitutes a large fraction of the atmospheric aerosols (Hallquist et al., 2009), and, therefore, knowledge on the formation and transformation of atmospheric SOA particles are needed for understanding and modelling the aerosol climate effects.

Gas-particle partitioning changes the composition and size of atmospheric aerosol particles. To capture these changes for SOA in models, parameterizations for saturation concentration ($C^*$) distribution of SOA constituents have been developed based on SOA growth experiments. SOA derived from oxidation of α-pinene is often used as a model system for atmospheric biogenic SOA. While the properties of such system have been the subject of many laboratory studies, there is still uncertainties regarding e.g. viscosity of the produced particles and volatilities of individual constituents. Vaden et al. (2011) and Wilson et al. (2015) found that SOA particles formed in ozonolysis of α-pinene evaporate slower than expected based on the volatility basis set (VBS) parameterization derived from SOA growth experiments. One possible explanation for such slow evaporation, especially at dry conditions, could be a semi-solid phase state of the particles and the resulting particle phase diffusivity limitations due to high viscosity of the particles. However, extremely low-volatile compounds, that are not included in the previous $C^*$ parameterizations but which have been detected in gas phase (Ehn et al., 2014) could also explain slower evaporation. Additionally, vapor wall losses may affect SOA experiments and cause uncertainty in derived SOA properties (Kokkola et al., 2014).

Here we investigate the evaporation of α-pinene derived SOA particles under dry and atmospherically relevant humidity conditions. We concentrate especially on the roles of the particle viscosity and the volatility distribution of compounds.

METHODS

SOA was generated by ozonolysis of α-pinene in a flow tube. A monodisperse particle population (diameter 80 nm) was selected from the flow tube with a differential mobility analyzer (DMA) and led to an evaporation chamber (volume 100 L) made of polished stainless steel. The particles were sampled from the outlet of the chamber for size measurements during the chamber filling. After the filling, the chamber was closed. Later the measurements were resumed after certain periods. Filling time was 20-40 minutes.
and the experiments extended up to few hours. Particle size change at short residence times (up to few minutes) was measured by bypassing the evaporation chamber and sampling from the DMA through stainless steel tubing. Particle size was measured with a Scanning Mobility Particle Sizer (SMPS). Chemical composition of the particles was measured with a High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS, hereafter AMS). Gas phase concentration of α-pinene was monitored with a Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-ToF-MS). The conditions in the flow tube were similar in all experiments. However, the sheath flow in the DMA and the evaporation chamber were conditioned to either dry, 40% RH or 80% RH to enable the investigation of SOA particle evaporation at different humidity conditions.

The measured evaporation rates, i.e. the particle diameter as a function of time, were interpreted using two evaporation models. In both cases, organic compounds were presented with an 8-bin VBS approach (Donahue et al., 2006) with $C^*$ values $10^{-3}$-$10^4 \mu g m^{-3}$. The first model, the evaporation model for liquid-like particles assumes well-mixed particles. It is based on the gas phase diffusion of vapor molecules arising from the difference between equilibrium vapor concentrations and the gas phase concentrations. The second model, the kinetic multi-layer model is a modified version of KM-GAP (Shiraiwa et al., 2012; Shiraiwa et al., 2013). It includes presentation of molecular diffusion also inside the particles and, therefore, takes into account the effect of particle phase viscosity. The Stokes-Einstein relation was used for calculating the particle phase diffusion coefficients from the particle viscosity. While the evaporation of organics was presented as dynamic process, water uptake by the particles was calculated in both models assuming an ideal solution and constant instantaneous gas-particle equilibration.

First, the liquid-like particle evaporation model was used for the 80% RH experiment, as the viscosity of α-pinene SOA particles is relatively low at this high humidity (Rembaum-Wolff et al., 2013). The model was fit to the measured evaporation by optimizing the initial particle composition (volatility distribution of the compounds in the particle phase at the beginning of the evaporation). After this, the multi-layer evaporation model was applied for the dry and 40% RH experiments together with different assumptions of particle viscosity. The initial particle composition derived from the 80% RH experiment was assumed to hold also for the dry and 40% RH experiments as the particles were formed in same conditions in all experiments.

**RESULTS AND CONCLUSIONS**

The particles evaporated much faster at 80% RH compared to dry conditions. At 40% RH the evaporation rate was only slightly faster than at 80% RH. If the only difference between the humidity cases would be water uptake and the resulting Raoult’s solution effect, then a slower evaporation would be expected at high RH compared to dry conditions. Therefore, our results suggest that the presence of water had also other effect than the dilution of a solution particle. The faster evaporation of particles at 80% RH compared to dry conditions is in agreement with the previous studies for α-pinene SOA evaporation (Vaden et al., 2011; Wilson et al, 2015). The similar evaporation rate at 40% RH compared to 80% RH is in disagreement with the previous study (Wilson et al. 2015) which reported almost same evaporation rate at intermediate humidity as at dry conditions.

According to the model simulations, at the beginning of the evaporation over 37% of the particle mass consisted of the low-volatile compounds with $C^* \leq 10^2 \mu g m^{-3}$. As the particles evaporated, the more volatile compounds evaporated first, leaving only least volatile compounds in the particles at the end of the experiments. However, based on the AMS measurements, O:C ratio stayed constant (0.55) throughout the evaporation. This suggests that the low-volatile compounds were not highly oxidized. Instead, the low-volatile compounds were possibly dimers, that have similar O:C as the corresponding more volatile monomers.

To match the observed evaporation curve with the model, we needed to assume a strongly composition dependent viscosity for the particles evaporating at dry and 40% RH conditions. The viscosities increased
along the evaporation, up to approximately $10^9$ Pa s (dry) and $10^8$ Pa s (40% RH), as the mass fraction of the least volatile compounds increased. At 40% RH the effect of the viscosity on the evaporation rate was, however, small, and we cannot exclude the possibility that uncertainties in water uptake calculations or experimental methods would explain the difference in modelled and measured evaporation rate at these intermediate RH without any viscosity effect. Our results suggest that under atmospherically relevant RH the effect of particle viscosity on evaporation of SOA particles derived from $\alpha$-pinene ozonolysis is small compared to the uncertainties in the volatilities of individual SOA constituents.

ACKNOWLEDGEMENTS

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AN INTRODUCTION TO THE IBAIRN FIELD CAMPAIGN

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Keywords: ORGANIC NITRATES, HOMS, NPF.

INTRODUCTION

The Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen Budget (IBAIRN) is a field campaign conducted by the University of Helsinki and the Max Planck institutes in August and September, 2016. The measurement site is located in the SMEAR II station in Hyytiälä, Finland. Scientific aims of IBAIRN include: 1) to examine the formation pathways of organic nitrates (ONs) from biogenic volatile organic compound (BVOCs) degradation during daytime/nighttime in the boreal forest; 2) to better characterize the role of ONs in new particle formation (NPF) events and secondary organic aerosol (SOA) formation; 3) to assess the contribution from soil emission and entrainment from free troposphere/nocturnal residual layer in providing NOₓ in ONs formation; 4) to evaluate the significance of two different termination pathways of photochemical cycle by comparing the formation of the different termination products (alkyl/peroxy nitrates and organic peroxides).

BACKGROUND

Atmospheric aerosols play a crucial role in the Earth’s radiation budget by altering cloud albedo and lifetime [Heintzenberg and Charlson, 2009], and have a strong influence on climate [Solomon et al., 2007]. Previous studies suggested that up to ~50% of the global cloud condensation nuclei (CCN) could be traced back to the NPF events [Kuang et al., 2009; Merikanto et al., 2009]. However, the exact mechanism of NPF is less understood. Though sulfuric acid and ammonia are considered as the key initiators for most nucleation processes, they are not capable to sustain the observed growth of the particles. Thus, low-volatile condensable organic vapors, which are produced by the oxidation of BVOCs such as α-pinene, are considered as one of the most likely explanation to the particle growth [Ehn et al., 2014; Kulmala et al., 2013; Riipinen et al., 2011]. These oxidation products, consisting of C₁₀ compounds and the respective dimers, are named highly oxidized multifunctional organic compounds (HOMs). One important group of HOMs, ONs, is less investigated but of high interest, for the following reasons: 1) the specific formation mechanism of ONs, especially in the presence of hydroxyl radicals (OH) and nitric oxides (NO) during daytime is still unknown [Yan et al., 2016]; 2) the role of ONs in NPF and secondary organic aerosol (SOA) formation, considering their assumed higher volatility compared to normal non-nitrate HOM molecules, remains an open question. Thus, better characterizations of atmospheric ONs are needed.

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 ONs with high oxidation states, as well as sulfuric acid. The third CI-API-TOF is specially modified to measure ground-level HO₂ and RO₂ concentrations. In addition, an iodide ion based ToF-CIMS [Lee et al., 2014] that has higher resolution and equipped with a filter inlet for gas and aerosol (FIGAERO) is also deployed to detect a broader group of both gas-phase and particle-phase species. VOCs are measured with a proton transfer reaction time-of-flight (PTR-TOF) mass spectrometer [Graus et al., 2010]. A high resolution time-of-flight aerosol mass spectrometer (HR-
TOF-AMS) [DeCarlo et al., 2006] is involved to measure the mass fraction of SOA. The concentration and size distribution of particles and ions are observed with a collection of instruments, such as particle size magnifiers (PSM), neutral cluster and air ion spectrometer (NAIS) and scanning mobility particle sizer (SMPS).

MPI deploy several instruments to measure nitrogen-containing gas phase species. Concentrations of peroxyacetyl nitrate (PAN), acetic acid and peracetic acid are measured with a quadrupole chemical ionization mass spectrometry (CIMS) using iodide ion source. Several cavity ring-down spectrometers (CRDs) are used to observe the concentrations of NO$_3$, N$_2$O$_5$, NO$_3$ reactivity, alkyl nitrates (RONO$_2$) and peroxy nitrates (RO$_2$NO$_2$).

Preliminary results from this campaign will be presented at the meeting.

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EFFECTIVE BVOCS EXCHANGE OF BOREAL FORESTS: EMISSIONS VERSUS IN-CANOPY SINKS

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Keywords: BVOC flux, BVOC deposition, air-canopy exchange model.

INTRODUCTION

The in-canopy concentration of biogenic volatile organic compounds (BVOCs) in a boreal forest is controlled by several processes. First, the vegetation emits a large amount of BVOCs, e.g., isoprene and monoterpenes (Guenther, 2002). Secondly, the emitted BVOCs in the air can be oxidized to the multifunctional oxidized volatile organic compounds (OVOCs) and finally degrade to carbon dioxide (CO2), condense onto particles or deposit to surfaces. Thirdly, the turbulent mixing at the canopy top also plays a crucial role in the exchange of BVOCs in a boreal forest canopy.

In this study, a multi-layer BVOCs dry deposition model has been newly implemented into a 1-dimensional chemical transport model SOSAA (a model to Simulate the concentrations of Organic vapours, Sulphuric Acid and Aerosols) (Boy et al., 2011) to investigate the in-canopy sources and sinks of BVOCs. The deposition model for BVOCs was proposed two decades ago (e.g., Wesely, 1989). However, only until recently the detailed single-layer deposition model of BVOCs have been applied to investigate the BVOCs fluxes (Nguyen et al., 2015) and the loss of secondary organic aerosol (SOA) (Hodzic et al., 2014). Therefore the newly implemented multi-layer BVOCs deposition model in this study can provide a new insight on the BVOCs exchange of boreal forest, which is also useful for estimating BVOCs fluxes at the canopy top. The new model can also be applied in large-scale models in future.

METHODS

The BVOCs dry deposition model is based on the ozone (O3) dry deposition model described in Zhou et al. (2016). For BVOCs, the effective Henry's law constant (H*) and the reactivity factor (f0) are required to compute some specific resistances, e.g., rmes (mesophyll resistance), rcut (cuticular resistance), rsoil (soil resistance) and rws (wet skin resistance) (Wesely, 1989). Here the intrinsic Henry's law constant (H) is used because H can also produce reasonable surface resistance values and the surface pH is usually not available to estimate H* (Nguyen et al., 2015). The H values of all species included in current model are obtained from the measurement data if available (Sander, 2015), otherwise they are computed with the software EPI Suite v4.11 (https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411). The reactivity factors are taken from three values 0 (non-reactive), 0.1 (semi-reactive) and 1 (reactive), which are suggested according to the categories of organic compounds (Wesely, 1989). Finally, the specific resistances for BVOCs are computed according to Wesely (1989) and Nguyen et al. (2015):
where R (0.082 atm M\(^{-1}\) K\(^{-1}\)) is the gas constant, T is the temperature. \(r_{\text{soil, SO2}}\) and \(r_{\text{soil, O3}}\) are the soil resistances for SO\(_2\) and O\(_3\), respectively. \(r_{\text{ws, SO2}}\) and \(r_{\text{ws, O3}}\) are the wet skin resistances for SO\(_2\) and O\(_3\). \(r_{\text{cut, O3}}\) is the cuticular resistance for O\(_3\). Besides the deposition, the emissions of BVOCs were calculated by MEGAN (the Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al., 2006), the chemical reactions were generated from MCM (Master Chemical Mechanism) v3.2 (http://mcm.leeds.ac.uk/MCM), the meteorology part was based on the 1-dimensional version of SCADIS (SCAlar DIStribution, Sogachev et al., 2002). More details of the model were described in Zhou et al. (2016).

**CONCLUSIONS**

The model was set up to simulate a whole month from August 1st to 31st in 2010. The normalized sources and sinks for different species during the whole month are shown in Fig. 1. Here Qturb represents the in-canopy concentration change of BVOCs due to turbulent transport, which can be positive (downward turbulent transport) as a source term or negative (upward turbulent transport) as a sink term. Qemis is the emission source. Qdepo is the deposition sink. Qchem is the total chemical gain and loss. 29 important compounds out of 1969 were analyzed in this study, their MCM names and common names are shown in Table 1.

For those compounds emitted from vegetation, e.g., isoprene (C5H8) and monoterpenes (APINENE, BPINENE, LIMONENE, Carene, OMT), Qemis is the dominant source. The net chemical production is only significant for ISOP34OOH and ISOP34NO3, which are oxidized from isoprene. While Qturb is the major source for all the other compounds. Deposition is the main sink for most compounds except OH, acetaldehyde (CH3CHO), MBO, isoprene, monoterpenes and sesquiterpenes (BCARY, OSQ). For the very reactive compounds, e.g., sesquiterpenes and OH, Qchem is the main removal mechanism. The emitted isoprene and monoterpenes inside the canopy are lost via turbulent transport to the air above the canopy.

The minor contribution from chemistry for O\(_3\) can also be seen from Fig. 1, which is consistent with the previous study (Zhou et al., 2016). Zhou et al. (2016) also analyzed the diurnal cycle of the chemistry contribution ratio with respect to the dry depotion process (Fig. 2), which showed that chemical removal approaches its largest contribution at nighttime, up to 9% of dry deposition. At daytime, the O\(_3\) production from the photochemistry can compensate up to 6% of dry deposition loss before 10:00 in the morning.

<table>
<thead>
<tr>
<th>MCM</th>
<th>Common</th>
<th>MCM</th>
<th>Common</th>
</tr>
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<tbody>
<tr>
<td>ACETOL</td>
<td>acetal</td>
<td>HNO3</td>
<td>nitric acid</td>
</tr>
<tr>
<td>CH3CHO</td>
<td>acetaldehyde</td>
<td>APINENE</td>
<td>alpha-pinene</td>
</tr>
<tr>
<td>CH3CO2H</td>
<td>acetic acid</td>
<td>BPINENE</td>
<td>beta-pinene</td>
</tr>
<tr>
<td>CH3CO3H</td>
<td>peracetic acid</td>
<td>C5H8</td>
<td>isoprene</td>
</tr>
<tr>
<td>CH3COCH3</td>
<td>acetone</td>
<td>MBO</td>
<td>2-methyl-3-buten-2-ol</td>
</tr>
<tr>
<td>CH3OH</td>
<td>methanol</td>
<td>OMT</td>
<td>other monoterpenes</td>
</tr>
<tr>
<td>HCHO</td>
<td>formaldehyde</td>
<td>LIMONENE</td>
<td>limonene</td>
</tr>
<tr>
<td>HCOOH</td>
<td>formic acid</td>
<td>Carene</td>
<td>delta3-carene</td>
</tr>
</tbody>
</table>
Table 1: List of MCM names and common names for chemical compounds.

<table>
<thead>
<tr>
<th>MCM Name</th>
<th>Common Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLYOX</td>
<td>glyoxal</td>
</tr>
<tr>
<td>C2H4</td>
<td>ethene</td>
</tr>
<tr>
<td>PINONIC</td>
<td>pinonic acid</td>
</tr>
<tr>
<td>PINIC</td>
<td>pinic acid</td>
</tr>
<tr>
<td>BCSO2OH</td>
<td>oxidized from BCARY</td>
</tr>
<tr>
<td>C151OH</td>
<td>oxidized from BCARY</td>
</tr>
<tr>
<td>H2O2</td>
<td>hydrogen peroxide</td>
</tr>
<tr>
<td>BCARY</td>
<td>beta-caryophyllene</td>
</tr>
<tr>
<td>OSQ</td>
<td>other sesquiterpenes</td>
</tr>
<tr>
<td>ISOP34NO3</td>
<td>oxidized from C5H8</td>
</tr>
<tr>
<td>ISOP34OOH</td>
<td>oxidized from C5H8</td>
</tr>
<tr>
<td>OH</td>
<td>ozone</td>
</tr>
<tr>
<td>OH</td>
<td>hydroxyl radical</td>
</tr>
</tbody>
</table>

Figure 1. Simulated contributions of the sources and sinks for different compounds within the canopy during August, 2010, normalized by the maximum stacked absolute values of either sources or sinks.

Figure 2: (a) The daily averaged production and loss caused by chemistry ($F_{chem}$, red) and dry deposition ($F_{depo}$, blue) for O$_3$. (b) The ratio between $F_{chem}$ and $F_{depo}$. Zero lines for $F_{chem}$ and the ratio are plotted as dashed lines.
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HOW TO QUANTIFY SIMILARITY OF AEROSOL MASS SPECTRA?

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Keywords: CHEMOMETRICS, MASS SPECTROMETRY, AMS, SIMILARITY METRIC.

INTRODUCTION

In analysis of mass spectrometric data it is often necessary to evaluate and quantify how similar a pair of mass spectra samples are. This applies to e.g. algorithm-based classification and identification of aerosol mass spectra. Often Pearson’s product-moment correlation “r” is used to describe mass spectral similarity, without giving the matter further consideration. In this work we wish to highlight the importance of suitable (dis)similarity metric selection, and additionally explore optimising data weighting, in an example case involving classification of deconvolved organic aerosol spectra with a simple clustering algorithm (k-means; MacQueen, 1967).

METHODS

We studied an example set of 81 unit mass resolution aerosol spectra, obtained with an Aerosol Mass Spectrometer (AMS; Jayne et al., 2000). The samples each contained a “fingerprint” mass spectrum of an individual air pollution episode measured at the rural background station, SMEAR II, in southern Finland. The pollution spectra were deconvolved from ambient measurements by a factor analytical model (Paatero, 1999), separating the pollution factors from the background.

For this work we tested the aptness of four dissimilarity metrics (Pearson correlation, dot-product cosine, squared Euclidean “distance” and Manhattan distance) for describing the (dis)similarity between the aerosol mass spectral samples. We conclude there are indeed differences between the metrics’ performances. Both ‘dot-product cosine’ and ‘Pearson correlation’ were found to produce similar, robust classification results, with ‘squared Euclidean’ dissimilarity providing satisfactory results.

We also explored the effects of applying non-uniform weight distribution to the mass spectral variables (m/z), as is commonly done and advocated for in many mass spectrometric applications outside of aerosol sciences (stein and Scott, 1994). Specifically we applied ‘mass scaling’

\[
\text{weight}_{i, \text{mass}} = (m/z)_i^{S_m},
\]

(Eq. 1)

where \(i\) are our mass spectral variables, and \(S_m\) is a mass scaling factor, as well as ‘intensity scaling’

\[
\text{weight}_{i, \text{intensity}} = \text{signal}_i^{1/S_i},
\]

(Eq. 2)

where \(S_i\) is a scaling coefficient for signal intensity.

Comparing to uniform weight distribution we find mass weighting with \(S_m\) of 1…2 enhances the aerosol chemotype classification while signal weighting appears detrimental to it in our case of normalized AMS spectra.
RESULTS AND CONCLUSIONS

We find that even a simplistic, unsupervised, classification algorithm such as k-means can, with optimized similarity metric and data weighting, reproduce classical organic aerosol speciation schemes.

Based on this (albeit limited) study, we would like to encourage metric and variable weight distribution optimization in connection to any data analytical tasks involving aerosol mass spectra classification or algorithm-based identification. We find that Pearson correlation seems a suitable metric for identification and classification AMS mass spectra, although some theoretical considerations would seem to favour dot-product cosine metric instead. The two seem to produce almost identical results in our tests. We also recommend exploring ‘mass scaling’ as a basis of weight distribution among variables, as in our case it does markedly enhance aerosol classification to aerosol chemotypes.

Further background, discussion and results of this work are available in the online manuscript, currently under review in Atmospheric Chemistry and Physics Discussions (Äijälä et al., 2016).

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