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Analytical expression for the gas/particle equilibration time scale and its numerical evaluation

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Keywords: Atmospheric aerosols, Gas/particle partitioning, Secondary aerosol formation

INTRODUCTION

A significant fraction of tropospheric aerosols is made by semi-volatile compounds (SVCs) that exist both in gas and particle phases in non-negligible amounts. A prominent group of SVCs are organic compounds (SVOCs) that are formed in the gas phase and subsequently partitioned into the aerosol phase via condensation.

In both modelling and experimental studies, it is often assumed that SVOCs reach thermodynamic equilibrium practically immediately, allowing for a straightforward estimation of the particle-phase concentration of SVOC(s). Also, characteristic time needed for a SVOC to reach the equilibrium can be evaluated using simple expressions presented in the literature (Seinfeld and Pandis, 2006). Our aim is to re-examine these time scales, and test the derived expression against a numerical model.

METHODS

Let us consider mass transfer of a vapour $i$ between the gas phase and monodisperse particle population. The particles are assumed to be spherical, having a diameter $d_p$, and to consist of a single, liquid-like absorbing phase. According to the condensation equation the mass transfer rate of $i$ between the gas and particle phases, $J_i$ can be expressed as follows:

$$J_i = K_1 (C_{gas,i} - x_i K_2)$$  \(1\)

where $x_i$ is the mole fraction of $i$ in the particle phase, $C_{gas,i}$ is the gas-phase concentration of $i$, $MW_i$ and $D_i$ are the mole weight and gas-phase diffusion coefficient of $i$, respectively, $\beta$ is the so-called Fuchs-Sutugin correction factor that accounts for non-continuum effects, $K_e$ is the Kelvin term, $C^0_{sat,i}$ is the saturation vapour concentration as a pure compound and $\gamma_i$ is the activity coefficient of $i$ in the solution. By assuming that only sink for gaseous $i$ is condensation onto particles, we derived an “e-folding” time scale based on eq. 1 that combines the expressions 12.133 and 12.147 presented by Seinfeld and Pandis (2006).

In order to test the accuracy of the derived time scale, we performed calculations with a model that simulates mass transfer between the gas and particle phases by solving equation (1) and the mass balance equation for $i$. The numerical timescale for equilibration, $t_{eq,num}$, is defined as a moment $t$ when the following criterion is met: $(x_{eq,i} - x_i(t))/x_{eq,i} < 1/e$, where $x_{eq,i}$ is the equilibrium mole fraction.

RESULTS AND CONCLUSIONS

Figure 1 shows a comparison of the analytical and numerical time scales for a series of Monte Carlo calculations where the key properties of $i$ were varied. As seen, the accuracy of the analytical expression depends strongly on $S$: an excellent agreement is reached when $S<1$ while it systematically overestimates the equilibration time when $i$ is non-volatile in a sense that $S>1$. To conclude with, the accuracy of the expression for the equilibration time scale depend not only on $C^0_{sat,i}$ alone, but also on the amount of $i$ present in the system.

REFERENCES

Chemical composition of submicron aerosol in PoValley in winter 2014

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Keywords: ACSM, chemical characterization, fine particles,

INTRODUCTION

In this study on-line fine particle aerosol chemical composition and optical properties were measured at San Pietro Capofiume (SPC) site in Po Valley, Italy in February 2014. The campaign was a part of the study conducted simultaneously at several different locations in Northern Italy. In this presentation only results from the SPC site are shown.

The SPC site is located at a background area approximately 30 km north-east from Bologna. The area is densely populated on its southern, western and northern sides. The Adriatic Sea is located approximately 40 km east from the site. Within the Po Valley there are many large industrial, urban and agricultural areas. The area has been identified as one of the hot spot places where pollutant levels remain high.

The aim of the study was to investigate the chemical composition of submicron particles in Po Valley in order to understand the reactions and transformations of pollutants coming from combustion sources, or from other processes, and to improve the assessment of potential health effects of particles.

METHODS

The aerosol chemical speciation monitor (ACSM, Aerodyne Research Inc.) was used to characterize non-refractory sub-micron aerosol species (NR-PM1: organics, nitrate, sulfate, ammonium and chloride) with the time resolution of 30 min. Black carbon and the light-scattering coefficient of particles were measured using multi angle absorption photometer (MAAP) and an integrating Nephelometer, respectively. The organic aerosol fraction was further investigated by using multi linear engine algorithm (ME-2) and the custom software tool SourceFinder (SoFI) to find different particle sources like traffic, biomass burning and cooking or similar chemical characteristics such as low-volatility (LV) and semi-volatile (SV) oxygenated organic aerosol.

CONCLUSIONS

The sum of measured aerosol chemical constituents varied from <1 μg m⁻³ up to 27 μg m⁻³ (Fig. 1). The major chemical components were organics and nitrate. The concentrations of organics and black carbon correlated well during the measurement campaign. Even higher correlation was found between mass fragment m/z=60, the tracer of biomass burning, and black carbon, indicating that the majority of the measured black carbon and a substantial amount of organic aerosol was formed via biomass burning processes. The diurnal variation of mass fragment m/z=60 and organics showed that their concentrations increased sharply after 16:00 UTC. The maximum nitrate concentration was achieved during morning hours.

ACKNOWLEDGEMENTS

This work has been conducted as part of the “Supersito” Project, which was supported and financed by Emilia-Romagna Region and Regional Agency for Prevention and Environment under Deliberation of Regional Government n. 428/10. This work was also supported by the Academy of Finland (Grant No. 259016).
Tire tread wear particles in ambient air - a previously unknown source of human exposure to the biocide 2-mercaptopbenzothiazole.

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Keywords: 2-mercaptopbenzothiazole, tire tread wear, urban air PM, human exposure

INTRODUCTION

A total annual loss of tire rubber has been estimated to \(10^7\) kg/year in Sweden (Ahlbom and Duus, 2003), which makes tire tread wear an important non-exhaust contributor to particulate matter <10 µm (PM\(_{10}\)), even if only few percent of the tire tread wear becomes airborne. Benzothiazoles are high production volume chemicals, in largest amount used as vulcanization accelerators in rubber production, but also as biocides and fungicides (Kloepfer et al., 2004). Benzothiazoles are biological active compounds that have been found to cause eye, skin and respiratory irritation and skin sensitization (Fishbein, 1999a, b). In addition, 2-mercaptopbenzothiazole (MBT) has shown potential mutagenic effects (Haroune et al., 2004) and is included in the European directive on biocides (The Commission of the European Communities, 2003). The aim of this present study was to investigate whether wear particles, i.e., tire tread wear and road surface wear could contribute to atmospheric concentrations of benzothiazoles and whether they could be a source of humane exposure to MBT.

METHODS

Different makes of automobile tires, authentic asphalt and airborne PM, all collected at the busy street Hornsgatan in Stockholm, Sweden were analyzed for their content of the commonly used benzothiazoles using a ultra-sonication assisted extraction and a high performance liquid chromatography – electrospray ionization mass spectrometry method (Avagyan et al., 2013).

CONCLUSIONS

PM\(_{10}\) contained on average 17 pg/m\(^3\) benzothiazole (BT) and 64 pg/m\(^3\) MBT, and the total suspended particulate (TSP) associated BT and 2-MBT concentrations were 199 pg/m\(^3\) and 591 pg/m\(^3\), respectively. This indicates that tire tread wear may be a major contributor of these compounds to urban air PM in Stockholm. Only BT was detected in the asphalt samples with a mean mass fraction 190 times lower than in tires, suggesting that road surface wear is a minor source of air particle associated BT. The contribution of tire tread wear particles to urban air PM\(_{10}\) and TSP at Hornsgatan was estimated to 0.7 and 5.5 %, respectively, using BT as a marker, which agree well with several other studies using other markers. MBT was determined in urban air PM for the first time in this study and its presence in inhalable PM\(_{10}\) implies that a large fraction of the population might be exposed to MBT from road traffic. The current knowledge of the risks associated with MBT exposure is scarce and a revision of the risk assessment is necessary.

REFERENCES

The Effect of Cloud Properties on Photolysis Rates and New Particle Formation: Results from the 3-D regional CTM PMCAMx-UF

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Keywords: cloud, new particle formation, PMCAMx-UF, photolysis rate

INTRODUCTION

Atmospheric new particle formation (NPF) has received increasing attention due to its possible impact on climate and human health. The solar radiation intensity as an important trigger for NPF is strongly affected by cloud cover, and the presence of clouds may therefore suppress H2SO4 production. To quantify the feedback involving aerosol formation, cloud dynamics, and climate response, the effect of clouds on aerosol formation needs to be understood. The impact of cloudiness on new particle formation has so far received relatively little attention.

METHODS

We use a regional-scale chemical transport model (PMCAMx-UF) to assess the impact of clouds on NPF and evaluate the importance of a detailed cloud representation for accurately simulating particle size distributions during NPF events. We use the three-dimensional chemical transport model PMCAMx-UF (Fountoukis et al., 2012) to simulate the emission, advection, chemical and microphysical processing, and deposition of both the number and mass of chemically specified particles over Europe for May 2008. PMCAMx-UF modifies the clear sky photolysis rates by applying a multiplicative factor (Ac). In this study, the model was updated by implementation of a more sophisticated approach Tropospheric Ultra-Violet and Visible (TUV) model (NCAR, 2011) to treat the cloud presence.

CONCLUSIONS

Figure 1 shows Adding a more sophisticated radiation parameterization, influences vertical distribution of H2SO4 and thus the origin of new particles in PMCAMx-UF suggesting constraining the source of new particles and role of vertical transport. Cloud perturbation of ground-level radiation and subsequent ground-level sulphuric acid production is not adequate to explain the sensitivity of modeled NPF to cloud properties.

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REFERENCES


The effect of organic aerosol material on aerosol reactivity towards ozone

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Keywords: heterogeneous reactions, aerosol aging, flow tube experiments, organics

INTRODUCTION

Heterogeneous reactions on aerosol particles play a significant role in trace gas cycles and alter the properties of aerosol particles. Low-diffusivity organic coatings can suppress these reactions (Shiraiwa et al., 2011; Zhou et al., 2011). Our aim is to better understand and quantify how the viscosity and phase state of organic aerosol matter affect gas-particle interactions. To this end, we study the reaction of ozone (O₃) on potassium iodide (KI) particles with different polyethylene glycol (PEG) coatings as a model system.

METHODS

We performed exploratory experiments with an aerosol flow tube setup at the University of Washington. Aerosol particles were generated by atomizing solutions containing varying amounts of KI and PEG, and inserted into the upper end of a laminar flow tube. O₃ was inserted into the tube through a movable, axial injector. Aerosol particle (surface) concentrations (S) and remaining O₃ mixing ratios were measured from the tube’s lower end. We determined the reaction rate k and the reactive uptake coefficient γ (k = Sωγ/4), either by varying the particle/O₃ interaction time by moving the injector or by measuring with and without aerosol particles.

We had to insert a filter after the tube to keep the particles from interfering with the optical O₃ detection method, and a dryer to reduce their reactivity after their collection on the filter. While this method worked well for pure KI particles, large losses of O₃ occurred on the filter after using particles that contained PEG.

PRELIMINARY RESULTS

Fig. 1 shows the remaining O₃ plotted against injector position during one set of experiments with pure deliquesced KI particles (≈ 125 nm avg. diameter) and with KI+PEG particles (coated with avg. ≈ 10 nm PEG 400). Clearly, the particles with added PEG are much less reactive; the γ value obtained from an exponential fit is about four times lower. Since PEG 400 is liquid at room temperature, this is a surprisingly large effect.

We performed a larger number of particle modulation experiments, where the aerosol particle production was switched on and off, with atomizer solutions with different KI and PEG concentrations. We expected that a larger PEG content in the solution would lead to thicker coatings and more suppression of the reactivity, but we did not find a clear trend in our data. Even a trend in the opposite direction could not be excluded. This is a very counterintuitive finding.

The accuracy of our results was likely affected by the O₃ losses on the filter before the O₃ monitor. Therefore, we aim to reproduce these experiments at UEF with an improved particle separation method.

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REFERENCES

Behavior of amine-enhanced nucleation in ECHAM5-SALSA

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Keywords: amine, general circulation model, nucleation

INTRODUCTION

Alongside the gas-to-particle conversion of sulfuric acid, gas-phase amines have recently been subject of many studies, which have shown that amines participate in nucleation (Erupe et al., 2011; Almeida et al., 2013; Kürten et al., 2014). Especially the results from the CLOUD (Cosmics Leaving OUtdoor Droplets) experiment indicate that amines enhance sulfuric acid-water nucleation several orders of magnitude (Almeida et al., 2013). In this study we use a parameterisation of amine-enhanced nucleation in a global aerosol-climate model ECHAM5-SALSA and explore the extent and behaviour of amine-enhanced nucleation.

METHODS

We have implemented a simple amine cycle into the aerosol-climate model ECHAM5-SALSA (Bergman et al., 2012). In the model, emissions of gas-phase amine are parameterised to produce global estimates (Schade and Crutzen, 1995; Ge et al., 2011). For oceanic emissions of amine, we use satellite retrieved chlorophyll-a concentration and 10-m wind speeds to determine the emission of gas-phase amine. We calculate emissions over land using the GEIA emission inventory for NH3 as a proxy. The modeled processes for the amine in the model are scavenging by hydroxyl radical (OH), dry and wet removal, particle uptake (by using condensation as a proxy) and nucleation. In the nucleation mechanism the enhancement is assumed to be caused by stabilization of sulfuric acid by amine molecules when the amine concentration exceeds 1 pptv (Almeida et al. 2013). Furthermore, the freshly nucleated particles grow only by addition of stabilized amine–sulfuric acid clusters.

CONCLUSIONS

Our simulations show that the amine-enhanced nucleation occurs mostly near the emission sources while activation-type nucleation is more evenly distributed. Main reason for the different spatial distribution compared to activation-type nucleation, when using the amine-enhanced nucleation, is the short 1.8 hour lifetime of gas-phase amine. With such a short lifetime, amine is not transported far from the sources and the local dynamics of the boundary layer play an important role. The local dynamics cause amine-enhanced new particle formation to produce two peaks in particle concentrations, one peak in the morning and one in the afternoon. The two-peaked daily cycle of amine-enhanced nucleation differs from the one with activation-type nucleation, which produces particles continuously through the daylight hours. The amine-enhanced new particle formation at midday is cut-off due to gas-phase amine concentration dropping below 1 pptv. Contrary to our expectations, this is not caused by scavenging of gas-phase amine by OH. Instead the reduction in gas-phase amine concentration results from vertical mixing with upper layers of boundary layer.

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REFERENCES


Absorption and chemical properties of combustion cycle resolved in-cylinder diesel soot

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Keywords: Diesel Soot, Soot Formation, Black Carbon, Absorption Ångström exponent

INTRODUCTION
Soot or black carbon (BC) emissions reduce air quality and increase the absorption of solar radiation in the atmosphere. Diesel engines contribute to approximately 20% of the global BC emissions (Bond et al., 2013).

Engine operating conditions alter the magnitude of particle emissions and may drastically change soot characteristics, such as light absorbance and scattering. The mechanisms and time scales of soot formation, oxidation and the transformation of soot properties in the cylinder are poorly understood.

In this project, in-cylinder particle properties are analyzed with the aim to improve soot emission modelling and to reduce toxic and climate relevant particle emissions from combustion engines.

METHOD
A heavy duty diesel engine was operated at a low load, 1200 rpm and at three levels of exhaust gas recirculation (EGR) corresponding to 21%, 15% and 13% inlet oxygen concentration (C(O₂)). A method based on a fast sampling valve was used to extract a small semi-continuous aerosol flow (1ppm) from the in-cylinder gas mixture.

The aerosols were extracted at well-defined stages of the combustion cycle, measured as the crank angle (CA) position after the piston top dead center (ATDC) at 0°C. The sampling resolution depends on the in-cylinder pressure, with a 1°C CA sampling window near 10°C (ATDC).

The diluted sample was analyzed with three on-line techniques: a Soot-Particle Aerosol Mass Spectrometer (SP-AMS), an SMPS and a 7-wavelength Aethalometer.

CONCLUSIONS
The observed in-cylinder BC mass concentration was found to be heavily dependent on the combustion cycle and EGR level (figure 1, main graph). At lower EGR, i.e. 21% and 15% inlet C(O₂), the soot concentration varies more than two orders of magnitude over the combustion cycle.

Furthermore, the oxidation of soot is very fast at low EGR resulting in low net soot emissions.

The absorption Ångström exponent (αabs) was determined at each sampled point of the combustion cycle. Late in the cycle, the αabs is low and the particles are “black” or graphite-like. At an early stage of combustion, there is an increase in particle “brownness” with high αabs, possibly due to absorbing organic carbon. Increasing the EGR also tends to result in more “brown” particles throughout the combustion cycle.

The SP-AMS analysis indicates that the increased particle brownness is associated with an increased polyaromatic hydrocarbon (PAH) to BC ratio (figure 1, sub-graph).

Figure 1: Aethalometer BC (880nm and 950nm average) at three levels of EGR (C(O₂)) against the combustion cycle (in CA). Sub-graph: Absorption Ångström exponents and PAH fraction normalized to BC (and peak) at 13% inlet C(O₂) against CA.

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REFERENCES
Skyvan flights during BAECC campaign

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Keywords: Airborne, mass spectrometry, CCN, GHG

INTRODUCTION

The Biogenic Aerosols – Effects on Clouds and Climate (BAECC, see webpage in references for details) field campaign was conducted to measure biogenic aerosols emitted from forests in order to determine their effects on clouds, precipitation, and climate. Finnish Meteorological Institute (FMI) contributed to BAECC campaign with airborne in-situ measurements using the Skyvan flying platform. Three vertical profiles of cloud and aerosol characteristics were done over the University of Helsinki’s Station for Measuring Ecosystem-Atmosphere Relations (SMEAR-II) and the second Atmospheric Radiation Measurement (ARM, see webpage in references for details) Mobile Facility (AMF2) placed at SMEAR-II during BAECC campaign from February through September 2014.

METHODS

A modified SHORT SC-7 Skyvan aircraft (Short Brothers and Harland Ltd, Northern Ireland, UK) suitable for various research purposes was used during BAECC campaign, see Fig. 1. It is a nonpressurized twin-engine turbo-propeller aircraft with a maximum operating distance of 1370 km and the maximum operating height of just over 3 km.

Figure 1: SHORT SC-7 Skyvan aircraft

There was a Cloud, Aerosol and Precipitation Spectrometer (CAPS, DMT, CO, USA) hooked to the right side of the plain. All the onboard instruments were connected to BMI Isokinetic Inlet System (Model 1200, Brechtel Manufacturing Inc., USA.). The onboard instruments included: the Soot particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research Inc., USA), the Single Particle Soot Photometer (SP2, DMT, CO, USA), the micro Aethalometer Model AE51 (AethLabs), the Cavity Attenuated Phase Shift Particle extinction monitor (CAPS PMex, Aerodyne Research Inc., USA), the continuous-flow stream wise thermal-gradient cloud condensation nuclei counter (DMT-CCNC) was used in this study, model No. CCN-100 (Droplet Measurement Technologies, Inc. DMT, USA) with the Constant Pressure Inlet (CPI, DMT, USA) set to 650 mbar., the condensation particle counter (CPC, model 3010, TSI, St. Paul, Minnesota, USA) and Picarro G1301-m (Picarro, Inc. Sunnyvale, CA USA) measured concentrations of CO, CO₂, CH₄ and H₂O.

The airborne measurements consisted of three flights, the first on September 4th from Malmi airport towards Hyytiälä SMEAR-II where two ascents from 332 to 3038 m.a.s.l were done between 13:40 and 15:11 UTC, then the airplane landed in Tampere airport. The second flight was done on September 5th morning from Tampere airport towards Hyytiälä SMEAR-II, where we did one ascent between 05:40 and 06:25 UTC and airplane landed back in Tampere airport. Third flight was done on September 5th around noon from Tampere airport towards Hyytiälä SMEAR-II, where we did one ascent between 09:20 and 09:55 UTC and airplane then continued to Malmi airport where landed.

ACKNOWLEDGEMENTS

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Inorganic Aerosol Production from Industrial Corona Discharge

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Keywords: corona discharge, industrial aerosol, emissions, inorganic aerosol

INTRODUCTION

Control of industrial pollution has been the focus of a large industry since the advent of clean air legislation in the 1970s.

Of the methods that available for emissions control, including pyrolysis and filters, Gas Phase Advanced Oxidation (GPAO) is a promising technology for the removal of low-concentration gas phase pollutants (Johnson et al., 2014). A technology that is competitive with GPAO is Low Temperature Plasma based techniques (Fridman, 2012).

As part of the gas phase treatment process in GPAO, pollution is oxidized by the OH radical. The products of this reaction, depending on the type of oxidation, typically have higher water solubility and lower vapor pressure encouraging the uptake onto existing particle surfaces or possible New Particle Formation (NPF). The same processes are presumed to be present in LTP, however the extent of the similarities are not clear. The quantification of the nanoparticle production in LTP and GPAO processes is to be addressed in this study.

METHODS

A simple corona discharge system is created using a high voltage power supply and a home-made corona discharge. The high voltage discharge is controlled by visual inspection of the produced corona and adjusting the voltage and distance between cathode and anode. The corona is generated by a negative high voltage power supply between 0-30kV and a maximum of 75\textmu{}A at 0V. Both copper and low-carbon steel electrodes are employed.

A reaction chamber contains the corona which is then connected to gas mixing manifold that allows the blending of multiple gases to produce a mixture to be treated by the corona. Gas phase species are detected with a Non-Dispersive Infra-Red (NDIR) chamber while particles are measured with a TSI 3076 Scanning Mobility Particle Sizer (SMPS).

Gaseous SO\textsubscript{2} flow is controlled by a 4 \textmu{}m critical orifice and diluted in 0.75 L min\textsuperscript{-1} dry, particle free laboratory air. Extra dilution is supplied by humidified laboratory air at 3.0 L min\textsuperscript{-1} leading to a net flux of 13.9 g m\textsuperscript{-3} of water through the chamber and a final RH of 80% and SO\textsubscript{2} concentration of 780 ppm. The chamber is 6 L in total volume giving a residence time of 96 seconds.

RESULTS

As can be seen in Figure 1, the size distribution changes markedly following the activation of the corona discharge. The initial background concentration is roughly bi-modal and results mainly from impurities in the DI water used to humidify the air stream. Following the activation of the corona discharge, the total concentration increases two orders of magnitude from $1 \times 10^4$ to $5 \times 10^6$ # cm$^{-3}$.

CONCLUSIONS

The high production of particles from the corona discharge, a proxy for LTP exhaust cleaning processes, indicates a large production of nanoparticles in a size range that is challenging to remove using the preferred Electrostatic Precipitators currently in use. Design of LTP systems for pollution reduction measures must address these nano-particles.

ACKNOWLEDGEMENTS

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Comparing ECMWF AOD with AERONET observations at visible and UV wavelengths

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Keywords: aerosols, ECMWF, validation, AOD

INTRODUCTION

The aim of this study is to evaluate the ECMWF UV/aerosol optical depth (AOD) model against ground-based measurements and further develop the UV Processor. The data used for the study is MACC reanalysis AOD and UV intensities for the period 2003–2006. The evaluation was done by comparing the model data with measurements from EUVDB (European UV Database), NSF (National Science Foundation) and AERONET (Aerosol Robotic Network). The ECMWF shortwave radiative transfer scheme provides the UV radiation at the surface for wavelengths between 280 and 400 nm. However, for this analysis, the wavelength ranges 290–320 (UVB) and 320–340 (UVA) were used. This is the first time when a global model such as the ECMWF is evaluated for the performance of AOD at a UV wavelength.

METHODS

For the comparison we use two different data sets, consisting of total AOD and AOD of five components (SS, DU, OC, BC, SO4). For the total AOD, we compare each hourly forecasted AOD in the MACC system at 340 and 500 nm with the average of the ground-based measurements within ±30 min from the model hour. This was done to have a temporal mean value from the pointwise measurements, which is arguably better comparable with the spatial mean represented by the model fields. However, the AOD comparison of five components is available only at 550 nm. In this case, the AERONET AOD500 values were extrapolated to AOD at 550 nm using

\[ \text{AOD}_{\text{aer},550} = \text{AOD}_{\text{aer},550} \times (550/500)^{-a}, \]

where \( a \) is the AERONET Ångström exponent of the wavelength range 440–870 nm. In this case, monthly instead of hourly averages were considered. For the comparison, the nearest model gridpoint to the actual validation site was used.

Statistics (relative mean bias, relative root mean square difference, correlation coefficient) were used for evaluating the performance of the hourly modeled versus measured AOD values.

CONCLUSIONS

The results show that the MACC system generally provides a good representation of the AOD on a monthly basis, showing a realistic seasonal cycle. The model is mostly able to capture major dust load events and also the peak months of biomass burning correctly. When comparing hourly AOD values, the model-measurement agreement is better for biomass burning and dust sites than for urban sites, with an average correlation coefficient around 0.90 for biomass burning sites, around 0.77 for dust sites, and below 0.70 for urban sites.

All sites included in the study show a relative mean bias at 340 nm smaller (or more negative) than that at 500 nm, indicating a strong wavelength-dependence in the performance of the AOD in the MACC system. A comparison against fine and coarse mode AOD of the AERONET indicates that this has to do with the size distribution of the model: generally, the ECMWF model overestimates the contribution by coarse mode particles.

ACKNOWLEDGEMENTS

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REFERENCES


Environmental radioactivity and air ion formation in the lower atmosphere

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Keywords: environmental radioactivity, radon, gamma radiation, air ions

INTRODUCTION

Ionising radiation released by natural radioactivity supplies the energy for the ionisation and excitation in the lower atmosphere. It is responsible for air ion production and, therefore, a key player in air conductivity, which is known as an indicator of air quality (Cobb, 1973). On the other hand, the energy expended in exciting trace gases in the atmosphere could contribute to the formation of neutral aerosol particles. Together with the charged fraction, these aerosol particles affect climate, human health and visibility (Poschl, 2005). Although vast investigations have been carried out in the field of natural radioactivity and in the field of air ions, the connection between natural ionising radiation and air ion formation is still poorly understood.

We, therefore, aim at investigating the relation between natural radioactivity and air ion formation as well as atmospheric electricity.

METHODS

This work is based on the environmental radioactivity and air ion measurements at Hyytiälä SMEAR II station (61°50′40″N, 24°17′13″E), located in southern Finland in a boreal forest (Hari and Kulmala, 2005). The environmental radioactivity at this site is monitored by a pair of Geiger-Müller counters for the beta emissions of radon decay and total gamma detector. Both of these instruments are deployed and owned by the Finnish Meteorological Institute (FMI). Air ions are measured with a Balanced Scanning Mobility Analyser (BSMA), Symmetric Inclined Grid Mobility Analyser (SIGMA) and Neutral and Air Ion Spectrometer (NAIS).

This first phase of the work seeks for reasons for the observed variations in natural ionising radiation and corresponding ion pair production, i.e. ion source rate. Then, by further comparing the ion source rate to the observed air ion concentration, an assessment on air ion balance will be performed. Finally, with the results of the assessment, possible improvement and refinement on the theory of air ion balance will be investigated.

CONCLUSIONS

Variations in natural ionising radiation in Hyytiälä SMEAR II station have been studied based on ambient data collected during 2000-2013. Seasonal and diurnal cycles in radon activity concentration and gamma dose rate were observed. The ion source rate derived from natural ionising radiation followed the same patterns as the natural ionising radiation. The median radon activity concentration was 2.2 Bq/m³ for 2000-2007, corresponding to an ion source rate of about 1.3 cm³/s. The gamma dose rate varied between 0.07 and 0.16 μSv/h for 2000-2013, which gave a median ion source rate of 9.1 cm³/s. The low gamma dose rate in winter and early spring was mainly due to the attenuation caused by snow cover. The patterns in radon activity concentration were probably connected to the stability of the atmosphere. Higher radon activity concentrations were observed when winds blew from the southeast direction. Soil conditions were found to influence the radon activity concentration. The diurnal cycles in the radon activity concentration resulted from the development of the boundary layer, which also made the diurnal features in total gamma radiation in summer and autumn distinguishable.

The source area of radon observed in the Hyytiälä SMEAR II station, along with further investigations connecting the natural ionising radiation with measured air ion concentration and atmospheric electricity, are under progress.

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REFERENCES

CCN activation of insoluble silica aerosols mixed with soluble pollutants

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Keywords: Silica, CCN activation, Mixture aerosols

INTRODUCTION

Flame-made (fumed) silica is one of the water insoluble anthropogenic particles emitted into the atmosphere by combustion processes. These particles can act as CCN if they acquire some deliquescent material. Extensive data and theories on CCN activation of completely soluble and insoluble particles exist but the CCN activation of coated particles has been investigated less. In this study laboratory measurements were conducted on CCN activation of insoluble silica particles mixed with soluble species. Also, we investigated the applicability of the current theoretical frameworks developed to describe this phenomenon.

MEASUREMENTS

Some laboratory measurements were performed on particle size distribution and cloud condensation nuclei (CCN) activity of silica particles mixed with ammonium nitrate (a salt), sucrose (a sugar) and bovine serum albumin known as BSA (a protein). The pure and mixed insoluble-soluble particles were produced by first dissolving them in deionized water, which was atomized and dried for further investigations. The agglomerated shape of the silica particles thus needed to be taken into account in the analysis of the CCN data. Therefore, the morphology of silica particles was investigated by APM measurements.

THEORY

κ-Köhler theory (Petters & Kreidenweis, 2007) was used to estimate the critical supersaturation of soluble particles. Critical supersaturation of pure silica particles, on the other hand, were calculated using the adsorption activation theory (Sorjamaa and Laaksonen, 2007; Kumar et al. 2011a). For mixed soluble and insoluble particles a model introduced by Kumar et al. (2011b) was used in the calculations.

CONCLUSIONS

CCN experiment results illustrated that the CCN activation of pure soluble and insoluble particles were in good agreement with κ-Köhler and adsorption activation theories. For mixed particles, we found that adding soluble species to the insoluble silica particles increased the CCN activity of these particles.

\[\text{Figure 1: Calculated and experimental critical supersaturations for silica - sucrose particles assuming constant (dashed lines) or varying (solid lines) soluble fraction with particle diameter.}\]

For the investigated species and particles, the theoretical calculations were governed by the fraction of soluble material instead of the adsorption properties of silica surfaces. We can thus conclude that if the soluble fraction can be reliably estimated, the existing theories can successfully describe the CCN activation of these kinds of particles. However, the soluble fraction is probably very sensitive to the way that the mixed aerosols are formed. In our wet-generated aerosol, the distribution of the soluble material on the aerosol size distribution was rather uneven, the soluble material accumulating in particles with mobility diameters smaller than 150 nm (Figure 2). These results highlight the need for controlled coating techniques.

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Finnish Meteorological Institute Aerosol Cloud Interaction Tube (FMI-ACIT)

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Keywords: tube, aerosol, clouds, CCN

INTRODUCTION

Clouds and their interaction with aerosol particles provide some of the greatest uncertainties in predictions of climate change. This is, in large part, because the properties of clouds and their formation processes are poorly understood. Several types of flow tube have been constructed and used in aerosol research (Lihavainen et al., 2001).

In this abstract a new device is introduced, Finnish Meteorological Institute Aerosol Cloud Interaction Tube (FMI-ACIT). FMI-ACIT is a multi-purpose instrument for investigating atmospherically relevant interactions between aerosol particles and cloud droplets under defined laboratory conditions.

METHODS

FMI-ACIT is based on principle of a laminar flow diffusion chamber (Lihavainen et al, 2001) and a laminar flow tube (Brus et al, 2010). It consists of three main parts: a saturator, a preheater and a condenser. In figure 1, the detailed setup of FMI-ACIT is presented.

![Experimental setup of FMI-ACIT](image)

The Cloud, Aerosol and Precipitation Spectrometer probe (CAPS, Droplet Measurement Technologies, Boulder, CO, USA) is connected at the bottom part of the condenser. Only CAS-DPOL probe from CAPS is used for particle detection.

RESULTS

First tests were conducted in order to investigate the most suitable conditions for FMI-ACIT. A flow-rate test was made to resolve what the most effective flow rate is. Particles of ammonium sulphate (250 nm) were produced and introduced into the FMI-ACIT through an aerosol inlet on the top part of the preheater. At low flows the particles are lost towards the tube walls and at high flows the aerosol does not grow to limits of detection of CAS-DPOL so the best conditions occurred between 8 and 9 lpm. A model was used to show the inner design of the condenser. System parameters (Ts, Tpr and Tc -temperatures of Saturator, Preheater and Condenser) were estimated to achieve supersaturation levels inside the tube. Figure 2 shows the calculated saturation as a function of radial (r) and axial (z) coordinates.

![Saturation profile inside the flow tube condenser](image)

Further laboratory campaigns will be conducted with FMI-ACIT in aerosol – cloud interaction area using aerosol with different hygroscopicity and shapes like desert dust, black carbon, sea salt on so on.

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Emulation of Cloud-Aerosol Indirect Radiative Effects (SA-ECLAIRE)

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Keywords: clouds, aerosol indirect radiative effect, emulation

INTRODUCTION

Aerosol indirect radiative effects are still responsible for the largest uncertainty in the IPCC’s radiative forcing, and are the only effects which still have a low level of confidence in our understanding (IPCC, 2013). One major challenge facing climate modellers is that cloud processes take place on a much finer scale than can feasibly be used in a regional or global model.

METHODS

At present, there are three main methods to represent clouds in climate models: a high-resolution model, with a fine resolution but a very limited domain; a traditional parameterization, where average values of environmental parameters across a full grid box are used to represent sub-grid processes; or a multi-model framework (MMF), where a two-dimensional model is nested within the grid-cells. The MMF greatly improves the representation of cloud-aerosol interactions within a climate model, but at significant computational cost. We propose using a different tool to represent cloud-aerosol processes: an emulator.

An emulator is a statistical tool which can be used to estimate a specific output of a high-resolution model to within a specified uncertainty. By carefully selecting boundary conditions to represent grid boxes in larger-scale models, an emulator of a cloud-resolving model can be created and implemented in a regional or global model. Emulators estimate the output of a model, based on a statistical analysis of outputs from simulations with known inputs. This method may reduce uncertainties in a range of cloud-scale processes, including calculations of aerosol indirect radiative effects, precipitation rates, and wet removal rates of aerosol.

CONCLUSIONS

We will describe the process of constructing an emulator from the WRF-Chem LES model to implement in the ECHAM-HAM-SALSA global climate model, together with any preliminary results.

Figure 1. A schematic representation of (a) high-resolution model, (b) conventional parameterization, (c) multi-model framework, and (d) emulator.

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Ice Nucleation Chambers for CRAICC

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Keywords: Ice Nuclei Chamber, PINC, ZINC, ice nuclei, CRAICC

INTRODUCTION

The importance of ice crystals in clouds for our climate is manifold: Their presence, number and shape influences the optical properties of clouds, the formation of precipitation and their lifetime. All of these aspects have an impact on the radiation balance and therefore on climate. Within the CRAICC project (Cryosphere-atmosphere interactions in a changing Arctic climate) we aim to investigate the ice nuclei properties of aerosols present in the artic region by continuous measurements at different Nordic field stations.

METHODS

Two new ice nucleation chambers are currently built based on the concept of the laboratory instrument ZINC (Zurich Ice Nucleation Chamber) and PINC (Portable Ice Nucleation Chamber), both being developed at ETHZ, Switzerland. The field instrument PINC has already successfully participated in a couple of laboratory campaigns (Chou et al, 2013; Kanji et al, 2013; Wex et al, 2014; Hiranuma et al, 2014) as well in field campaign (Chou et al, 2011). Our improved PINC has two portable refrigerant compressors to directly cool the walls of the chamber without the use of an intermediate cooling liquid. In this configuration, the instrument is able to measure ambient ice nuclei (IN) concentrations at conditions as cold as -40°C and relative humidities exceeding water saturation. Our improved PINC has a longer ice nucleation chamber (1 meter) similar to the ZINC.

CONCLUSIONS

A successful collaboration between ETHZ and the CRAICC partners has led to technology transfer for the manufacture of the two Ice Nucleation Chambers. An inter-comparison prior to their first campaign is scheduled in spring 2015. The status of the ice chambers, their operational field modes as well as their improvement will be presented during this meeting.

ACKNOWLEDGEMENTS

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Insights into the formation pathways of extremely low-volatile organic compounds (ELVOC) from monoterpenes

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Keywords: ELVOC, mass spectrometry, oxidation

INTRODUCTION

Extremely low-volatile organic compounds (ELVOC) were recently observed to form at high yields from the oxidation of certain important monoterpenes, and their impact on secondary organic aerosol (SOA) formation is expected to be considerable (Ehn et al., 2014). The formation of these highly oxidized molecules was believed to be based on autoxidation, where intramolecular H-atom abstractions in peroxy radicals are followed by addition of molecular oxygen to form a new, more oxidized, peroxy radical.

A more detailed understanding of the exact formation pathways of ELVOC from different precursors is needed in order to fully quantify their atmospheric importance under varying ambient conditions. Here, we have conducted follow-up studies on the formation of ELVOC and their precursor peroxy radicals in flow tube experiments using both monoterpenes and surrogate compounds.

METHODS

Our flow tube studies were conducted both at the University of Helsinki as well as in the Leibniz Institute for Tropospheric Research in Leipzig, Germany. Instrumentation used during the experiments included a proton transfer mass spectrometer (PTR-MS) for VOC concentration analysis and a nitrate ion based chemical ionization mass spectrometer (CI-API-TOF, Jokinen et al. 2012) for RO2 and other low volatility product detection. The identified ELVOC were all detected as nitrate clusters.

CONCLUSIONS

We were able to show that for the abundant monoterpane limonene, peroxy radicals with a wide range of oxidation states formed within seconds after reaction with ozone (Jokinen et al., 2014). Radicals with 6, 8, 10 and 12 oxygen atoms were detected, in line with the hypothesis of oxidation taking place through subsequent O2 additions. Similar radicals were detected also from the atmospherically most abundant monoterpane α-pinene, as well as at two different European field sites, highlighting the wide importance of these compounds.

In order to gain a better understanding of the exact step-by-step progression of this oxidation, we used a surrogate compound cyclohexene, which contains an endocyclic double bond which has been found to greatly facilitate autoxidation during ozonolysis. The simpler (symmetric) structure of cyclohexene also allowed us to perform quantum chemical calculations to support our experimental findings. The most favourable sites for H-atom abstraction were calculated, and all the predicted ELVOC structures could be identified in the cyclohexene ozonolysis mass spectrum, including C6H8O9 with an O:C ratio as high as 1.5. Furthermore, by using heavy water (D2O) in our flow tube to exchange labile hydrogen atoms, we were able to confirm that hydroperoxide functional groups, as expected, explained the majority of the oxygen in the ELVOC molecules (Rissanen et al., 2014).

Nevertheless, there are still open questions on how exactly the H-atom abstraction can progress as far as has been observed for the bicyclic α-pinene, and future work will focus on trying to shed light on this issue.

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Quantitative Determination of Reaerosolization of Anthrax and Its Surrogates from Representative Outdoor Surfaces

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Keywords: bioaerosol, reaerosolization, anthrax simulant

INTRODUCTION

A release of Bacillus anthracis (Ba) spores is a serious public health risk that would create many challenges for authorities, including the risk of ongoing exposure due to reaerosolization. Ba has the potential to reaerosolize after a release, but there is a lack of quantitative information that can be used to predict the reaerosolization risk to the public.

The United States Department of Defense (DOD), Department of Health and Human Services, Department of Homeland Security (DHS), and Environmental Protection Agency (EPA) partnered through the Scientific Program on Reaerosolization and Exposure (SPORE) with the primary objective of understanding Ba reaerosolization to inform response and mitigation decisions that will reduce the risks associated with an outdoor Ba release.

This part of the SPORE effort was dedicated to developing a methodology to quantify Ba and surrogate reaerosolization capable of producing reproducible results when conducted in independent laboratories. The two goals of this research were to quantify Ba spore reaerosolization from outdoor surfaces and to determine the suitability of B. thuringiensis var. kurstaki (Btk) and B. globigii (Bg) as surrogates for Ba in reaerosolization research.

METHODS

The test variables selected from a large number of potential variables were as follows: spore type (Btk, Bg, and Ba [Ames strain]), spore deposition method (wet and dry), jet velocity, surface material (asphalt, concrete, and glass), and roughness level within each surface material. The authors designed and constructed chambers for wet and dry deposition of spores onto surface materials and a small reaerosolization wind tunnel for conducting controlled reaerosolization experiments.

Computational fluid dynamics (CFD) modeling was used in the design process of the deposition chambers to achieve uniform surface coating of spores. The design of the wind tunnel was based on CFD modeling of particle transport under the influence of a slotted jet moving over the surface of a coupon of the selected surface material uniformly coated with spores. The wind tunnel was designed to maximize collection of reaerosolized spores through a flow transition unit onto four sample filters.

Reaerosolization tests using surrogate spores (Btk and Bg) were conducted at the EPA facility in Research Triangle Park, NC, USA. Replicas of the deposition chambers and small wind tunnel were constructed and sent to the DOD facility at Dugway Proving Ground (DPG), UT, USA. Tests using Btk and Ba-Ames spores were conducted in a Biosafety Level 3 laboratory. Reaerosolization data for both wet- and dry-deposited Btk were compared between the EPA and DPG laboratories. No statistically significant differences were found between the data from the two laboratories, validating the equivalence of experimental equipment and methods.

CONCLUSIONS

The experimental data showed no statistically significant differences in reaerosolization between Btk and Ba-Ames spores for either wet or dry deposition. Bg spore reaerosolization was 79% lower than the average for Btk and Ba-Ames. Wet-deposited spores reaerosolized significantly less than dry-deposited spores under the same experimental conditions. The results showed more spor reaerosolization from concrete than from asphalt or glass under the same experimental conditions.

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Evaporation Kinetics of Secondary Organic Aerosol Generated from Alpha-Pinene Oxidation

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Keywords: secondary organic aerosol, particle evaporation kinetics, ELVOCs

INTRODUCTION

Evaporation kinetics of secondary organic aerosol (SOA) cannot be fully explained by gas-particle partitioning models (Vaden et al., 2010). This seemingly aberrant behavior could be explained by 1) diffusional limitations to particle mixing that prevent gas-particle equilibrium, 2) the presence of extremely low volatility organic compounds (ELVOCs) that are not accounted for in models, or 3) some combination of these two phenomena. Models assume that SOA are liquid, but in reality they exist as an amorphous solid (Virtanen et al., 2010). Thus the particle phase could create diffusional limitations to particle mixing. On the other hand, ELVOCs are produced as oxidation products of biogenic emissions and contribute significantly to SOA production (Ehn et al., 2014). These low vapor pressure compounds are not included in models. This study investigated which of these phenomena could best explain measured particle evaporation kinetics of SOA generated from alpha-pinene oxidation.

METHODS

SOA was generated using a flow tube reaction chamber. Alpha-pinene was introduced to the flow chamber with a diffusion system and oxidized with ozone in the absence of light. Monodisperse SOA were introduced into a particle evaporation chamber with a differential mobility analyzer (DMA). The particle size distribution was monitored over the five to eight hours. The process was repeated for three different sizes of monodisperse particles: 80 nm, 100 nm, and 120 nm. The size-selecting DMA was run in both closed and open loop configurations to compare results between the two settings. A schematic of the set-up is shown in Figure 1.

Volatile organic compounds were measured in the particle evaporation chamber with a PTR-MS and CIMS. The PTR-MS measured higher volatility VOCs. The CIMS measured semi-volatile organics and ELVOCs with acetate chemical ionization and nitrate chemical ionization respectively.

Figure 1: Schematic of the laboratory set-up for generating SOA and measuring particle evaporation kinetics.

CONCLUSIONS

Particle evaporation kinetics were compared with results from Vaden et al., (2010). When the DMA was run in the closed loop configuration, results were similar to those presented by Vaden and colleagues. However, when the DMA was run in the open loop configuration, particles evaporated much more quickly. However, even in the open loop configuration, particles did not evaporate as quickly as gas-particle partitioning theory predicts. Observations of particle evaporation kinetics and gas-phase composition were used in process models to investigate reasonable explanations for the observed behaviour.

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REFERENCES


Climate change, air quality health effects across Europe – sensitivity to climate, anthropogenic emissions, population and building stock

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Keywords: Climate change, integrated assessment, air pollution, particulate matter, health impacts, infiltration

INTRODUCTION

Ambient air pollution has been shown to be a major public health concern in Europe (Lim et al., 2012). Future changes in population exposures to ambient air pollution are inherently linked with long-term trends in outdoor air quality, but also with changes in the building stock. Moreover, the burden of disease is further driven by the ageing of the European populations. This study aims to assess the impact of changes in climate (CC), emissions, building stocks and population on air pollution related human health impacts across Europe.

METHODS

An integrated model is used to test how sensitive the final health outcome is to changes in the main input data. The system connects global (ECHAM5) and regional (RCA3) climate models with two Chemistry-Transport Models (CTMs) DEHM and MATCH.

In this study projected future levels of both ozone and particulate matter are used as inputs to the Economic Valuation of Air pollution (EVA) model system for an integrated assessment of the related exposure and health effects.

The Nordic region is studied in detail as the impact of projected changes in the building stock, and hence in the infiltration rates, may impact the exposure to air pollution. The EU Directive on Energy Performance of Buildings requires for example that all new buildings inside the Nordic region will comply with nearly zero energy standards by 2020 and this will impact the actual exposure. Future projections of NH3 emissions from the ECLAIRE project are also included in the calculations. These estimates indicate an increase in NH3 emissions from the agricultural sector by up to 40% due to climate change. We include a scenario using these new emissions to evaluate if increased emission of ammonia due to climate change might have an impact on the related health effects. The integrated system and proposed analysis will form a basis for improved assessment of air quality and future health effects.

CONCLUSIONS

Impacts of CC alone are small. Substantial reductions are expected concerning SOx (up to 85% by 2080) and NOx (64%) emissions, leading to lower PM2.5 concentrations in the ambient air over the whole Europe. This is projected to lower the chronic mortality caused by ambient PM air pollution from 300-400 thousand annual deaths (estimates varying by model) to 50-100 thousand (factor of 4-6). In addition, in Nordic countries the improving energy efficiency of buildings is further reducing population exposures indoors by almost an additional factor of 3 by 2100. The impact of emission reductions in the Nordic countries is even larger, and the chronic mortality is expected to decrease from 8 000-10 500 (estimates varying by model) to 1 800-2 000 (by a factor of 4-5) by 2080.

More detailed analysis on the impact of emission profile changes on the composition of PM as well as particle size dependency of the building tightness and new ventilation systems is needed and some preliminary considerations are presented in a parallel paper.

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REFERENCES

Lidar observations of free tropospheric aerosol layers and their contribution to columnar aerosol optical depth in South Africa

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INTRODUCTION

Despite the fact that South Africa is one of the most affected countries with regard to aerosol load, due to various natural and anthropogenic activities, long-term studies of atmospheric aerosols over the region are limited. Moreover, in previous studies the optical properties of aerosols have been studied by means of sun photometers, in situ data (Laakso et al., 2012) and satellite observations. Thus there is a clear need for vertically resolved observations with advanced multiwavelength lidars.

In this study we present one year Raman lidar data that have been performed over Highveld in South Africa. The data have been analysed in regard to free tropospheric aerosol layers and their contribution to the columnar aerosol optical depth (AOD).

METHODS

A multi-wavelength Raman lidar PollyX was operated remotely at Elandsfontein (26°15’S, 29°26’ E, 1745 m a.s.l.) in South Africa from December 2009 to January 2011. The range-resolved backscatter signal of elastic lidar contains information that can be used to derive the height of aerosol layers. The gradient method was applied to determine the bottom and top layer heights of the aerosols in the free troposphere (FT). Planetary boundary layer top heights were retrieved from the lidar backscatter signal at 1064 nm using the Wavelet Covariance Transform method (Korhonen et al., 2014).

CONCLUSIONS

The AOD in the boundary layer and the FT at 355 nm is estimated and presented in Figure 1 (a). The boundary layer AOD is only indicative. The same seasonal pattern is observed for the AOD at 355 nm in the boundary layer and the FT, i.e. larger AOD values measured during late July, August, September and October in the boundary layer and the FT. The percentage contribution of free tropospheric AOD to the total AOD is presented in Figure 1 (b). Large variations of the contribution of free tropospheric AOD to the total AOD are observed for the period investigated, with a mean value of 46%. The largest monthly contribution of 92% is observed in October. The period with increases in columnar, free tropospheric and boundary layer optical depths coincides with higher wind speeds and an increase in biomass burning activity in South Africa (not shown here). Higher wind speeds could lead to an increase of biomass emissions from region further away from Elandsfontein.

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REFERENCES

Use of Heat Exchanger for Efficient Fine Particle Precipitation in Small-Scale Combustion

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Keywords: Heat exchanger, fine particle, thermophoresis, thermodynamics

INTRODUCTION

There is a need to develop feasible PM reduction methods for small-scale biomass combustion installations due to their high PM emissions. In this work, we evaluated the potential of a novel prototype small-scale heat exchanger (PHX) designed for high particle emission reduction. In addition, the role of the different deposition mechanisms in such an application was studied.

METHODS

The PHX was installed in the combustion reactor which consists of a 40 kW solid fuel burner and a ceramic insulated combustion chamber. The PHX was equipped with water scrubbing system to keep the heat exchanger walls (HX) clean. The temperatures of a flue gas and water upstream and downstream the PHX were monitored continuously as well as pressure drop over the PHX. The flue gas composition was analyzed with FTIR (Gasmet) and single gas analyzers (ABB) which continuously measured H2O, CO2, CO, O2 and NOx. The condensate which was collected in the bottom of PHX was weighed and later on analyzed for the content of inorganic compounds.

Experiments with a PHX were performed for optimal fine particle precipitation. The HX was operated in two different modes: floor heating and high temperature heating with incoming and outcoming water temperatures of 24 – 26 °C and 54 – 58 °C, respectively. Reference measurements were carried out with a conventional tube HX.

The experimental results were interpreted with simulations describing thermodynamics and fine particle dynamics in the HX system. In addition, the effects of a scrubbing unit, on keeping the HX walls clean, were measured.

CONCLUSIONS

The study shows that by optimizing the dimensions of a HX the particulate emissions can be decreased considerably in small-scale heating appliances operated with biomass fuels. In this study PM1 precipitation efficiencies between 45 and 48 % were achieved, depending on the applied heating water temperatures. Furthermore, due to recovering of latent heat of water vapour in the flue gas through the HX the whole system efficiency is considerably higher than when using a conventional small-scale tube HX. Therefore, the PM1 emissions as well as gas emissions per generated energy unit are further reduced in comparison to a conventional tube boiler.

All in all, the PHX replaces a part of the conventional boiler system; it is also a cost-efficient alternative for emission reduction when compared to other secondary emission reduction methods. The method is especially suited for a condensing boiler application due to the fact that the condensed water film naturally helps to keep the HX walls clean. The method can also be utilized as a part of a low-emission combustion system, for example, in combination with an electrostatic precipitator.

Figure 1. Chemical composition of the PM1 emissions with different prototype heat exchanger and reference boiler setups.

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High-speed fabrication of superhydrophobic nanocoating by Liquid Flame Spray

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Keywords: aerosol synthesis, Liquid Flame Spray, nanoparticles, nanocoatings

INTRODUCTION

Liquid Flame Spray (LFS) is an aerosol synthesis method for production of nanoparticles and nanostructured coatings. High-speed fabrication of nanocoated surfaces has been an issue for decades. We present high-velocity roll-to-roll fabricating of superhydrophobic surfaces by LFS. With paperboard line speeds up to 300 m/min, method gives promising results in pilot scale and shows a great potential for up-scaling.

METHODS

LFS is a versatile method for synthesizing nanoparticles. In LFS method, liquid precursor solution is fed via burner nozzle to a turbulent hydrogen-oxygen flame. Through various aerosol processes, nanoparticles are formed (Haapanen et al.). With variable process parameters, nanoparticle production rate, size and rate of agglomeration can be fixed on desired level. In this study, TiO₂ nanoparticles were deposited on paperboard surface in roll-to-roll process. LFS-made TiO₂ nanocoating is known to produce superhydrophobic surface on paperboard with the line speed of 50 m/min (Aromaa et al., Teisala et al.). Precursor solution was prepared by mixing titanium(IV) isopropoxide (TTIP) and isopropanol. Produced nanoparticles are analyzed in aerosol stage by SMPS and as deposits on paperboard surface by SEM. Wetting behavior of nanocoated paperboard surface is determined as water contact angle values, measured by goniometer. Mass of deposited nanoparticles has been evaluated by inductively coupled plasma mass spectrometry (ICP-MS). Yield of the coating process is determined from ICP-MS results.

CONCLUSIONS

Roll-to-roll line speeds from 50 m/min to 300 m/min are demonstrated succesfully. Results of water contact angle measurement 1 day after the coating process are displayed in Figure 1. Results show high level of hydrophobicity even with line speed of 300 m/min. According to these results, LFS is a competitive method for fabricating superhydrophobic TiO₂ nanocoatings for paperboard in large scale. Primary particle size for TiO₂ deposits is mainly 20-50 nm, verified by SEM and TEM analyses.

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REFERENCES


Carboxylic acid oxidation products from limonene ozonolysis and their role in SOA formation

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Keywords: Limonene, CIMS, Carboxylic acids, SOA

INTRODUCTION

Low vapor pressure products from the oxidation of volatile organic compounds (VOC) contribute significantly to atmospheric aerosol particles (Hallquist et al., 2009). Carboxylic acids are one class of organic compounds that plays an important role due to their low vapor pressure (Salo et al., 2009) and their role in SOA formation from limonene was elaborated in a recent modelling study (Pathak et al., 2012). According to our model, limonene-ozonolysis produces significant amounts of carboxylic acids such as limonic acid, limononic acid and limonalic acid together with the multifunctional compound 7-hydroxy limononaldehyde (Pathak et al. 2012). The model showed that the product distribution was affected by changes in both OH and ozone concentrations, which partly explained the observed changes in volatility, but was strongly dependent on accurate vapor pressure estimation methods.

METHODS

These findings have now been explored further by on-line mass spectrometry analysis using a high resolution chemical ionization mass spectrometer with an ionization scheme that allows for the quantification of carboxylic acids. All experiments were conducted in the same laminar flow reactor, G-FROST, where limonene was oxidized via ozonolysis under controlled conditions, stable humidity and temperature.

CONCLUSIONS

Figure 1. shows the effect of limonene concentration on SOA mass. The SOA mass gradually decreases as the limonene concentration is reduced. Figure 2. shows the selected mass to charge ratios corresponding to limononic acid and 7-hydroxy limononaldehyde (m/z 183), ketolimonacic acid (m/z 171), limonic acid and ketolimonacic acid (m/z 185) and limonic acid (m/z 169) which are used to illustrate the changes during the decrease in limonene concentration. The distinct differences in trend illustrate the non-linearity in processes occurring during the oxidation via ozonolysis of limonene.

Figure 2. The effect of decreasing limonene concentration on the oxidation products.

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References


Figure 1. The effect of decreasing limonene concentration on produced SOA mass.

Figure 2. The effect of decreasing limonene concentration on the oxidation products.
Century wide energy efficiency road map for buildings and impact on particle size specific PM infiltration

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Keywords: Climate change, energy performance, particulate matter, health impacts, infiltration

INTRODUCTION

Particulate matter (PM) has been estimated to cause substantial health losses in Europe and globally in 2010 (Lim et al. 2012). Climate change (CC) and mitigation policies are changing the atmospheric conditions, PM emissions and composition and tightness of building stocks (Geels et al., 2014). Many research groups have attempted to quantify the impacts of CC and changes in emissions on the ambient air quality. Much less attention has been put to the impacts of energy policies such as the European Energy Performance of Buildings Directive on the human exposures.

The current work aims at using the objectives set for the European building stocks in the Energy Roadmap to project potential changes in the i/o ratio of particulate matter pollution originating from outdoor air. Specifically we aim at characterizing the particle size dependences.

METHODS

We have previously developed a mass-balance model for estimating PM2.5 infiltration in existing building stocks in Helsinki and reviewed similar relationships in a number of other European cities (Hänninen et al., 2004, 2011). In Helsinki we have further applied an aerosol physics-based particle size dependent estimation (Hänninen et al., 2013). In this work we combine these models with characterization of the building stocks, accounting for the removal and renovation rate of existing buildings (2% a⁻¹) and improvement of building tightness as proposed by the European energy policies (EC, 2010, 2012).

We account for the residual old building stock, the mean air flows through mechanical ventilation systems assumed to be used in all new and renovated buildings that follow the Energy Efficiency for Buildings requirements, and estimate the remaining air infiltration through the building envelopes to calculate the effective resulting PM2.5 infiltration rates for the Finnish building stock.

CONCLUSIONS

The potential impact of building tightness is almost as large (-49%) as the current estimates for impact of climate change and changes in the anthropogenic emissions together (-60%).

While outdoor concentrations are estimated to be gradually decreased during this century, this development is substantially strengthened for the indoor concentrations of ambient aerosols by the decreasing infiltration.

The indoor concentrations are especially lowered for ultrafine (Dp<100 nm) and coarse (Dp>1 µm) sizes meanwhile the accumulation mode consisting of secondary inorganic particles is less affected. This means that the future projections of health effects are especially sensitive to the estimates of precursor gas emissions and the composition specific toxicity of nitrate particles.

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REFERENCES

Hygroscopic growth and critical super-saturation of limonene-derived organosulfates and their mixtures with ammonium sulfate

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Keywords: Aerosol, organosulfates, cloud condensation nuclei, hygroscopic growth

INTRODUCTION

Atmospheric aerosols have the ability to act as cloud condensation nuclei (CCN), initiating the formation of clouds and thereby influencing the climate system (Albrecht, 1989). The ability of aerosols to act as CCN depends on particle size and chemical composition (Lohmann and Feichter, 2005).

Organosulfates (OS), e.g. sulfate esters, have been observed as constituents of secondary organic aerosols in numerous atmospheric environments, even as far as the Arctic, where OS have been found to comprise 7-15% of total organic matter and 9-11% of submicron organic matter in two independent studies (Frossard et al., 2011; Hansen et al., 2014). However, the properties of particulate OS have not yet been investigated.

In this study limonene-derived organosulfates with a molecular weight of 250 Da (L-OS 250) were synthesized and the hygroscopic properties of these OS and their mixtures with ammonium sulfate (AS) were examined through a series of laboratory experiments.

METHODS

Six solutions of L-OS 250, AS and mixtures hereof were prepared in de-ionized water. Each of the solutions was used to generate aerosols by atomization for measurement of hygroscopic growth and critical super-saturation using a unique setup allowing simultaneous measurement of the two properties.

Following atomization the aerosol was dried and the aerosol flow split into two lines. One going to a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA, fifth generation University of Helsinki) for measurement of hygroscopic growth and the other going to a Cloud Condensation Nuclei counter (CCNC, DMT model CCN-100) for measurement of critical super-saturation.

The hygroscopic growth was measured for particles of four sizes (30 nm, 60nm, 100nm and 145nm) at four different relative humidities (80%, 85%, 90% and 93%) and the CCN activation was measured at 13 different super-saturations (SS, from 0.1% to 1.3% in steps of 0.1%).

CONCLUSIONS

Our measurements at sub-saturated conditions showed that L-OS 250 experience a weak hygroscopic growth. The growth factor increased from approximately 1.0 (no growth) to 1.18 when the relative humidity increased from 80% to 93%. This trend was observed for all four particle sizes investigated. From the measurements at super-saturation it was found that L-OS 250 can activate into CCN, however the critical diameter for activation was found to be significantly larger than for pure AS at all investigated super-saturations.

The observed growth factor as well as the critical diameter for CCN activation of the mixed L-OS 250/AS particles were dominated by the properties of AS. For particles where the mass fraction of AS ≥20% the observed growth factors and critical diameters were equal to pure AS.

Results from measurements of surface tension and further analysis of the data will be included in the presentation.

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Determination of Particulate Organic Nitrate Formation by AMS

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Keywords: Forestland-urban mixed region, organic nitrate aerosol, AMS.

INTRODUCTION

Particulate organic nitrate can be formed from nocturnal oxidation of anthropogenic and biogenic volatile organic compounds (VOCs). The Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) provides the possible solution of measurement of ambient organic nitrates by the advantage of its fast data acquisition, low detection limit, and specially the ability of separation of ions with the same nominal mass spectra and facilitates the better identification of aerosol components (e.g. N-containing compounds).

METHODS

The measurements were carried out during the Puijo Cloud Experiment 2010 campaign (PuCE 2010) (Hao et al., 2014). The station is located on the top of Puijo tower in a boreal forestland-urban mixed region in Kuopio, Finland. The chemical composition and mass size distributions of ambient aerosols were measured by Aerodyne high-resolution time-of-flight Aerosol Mass Spectrometer (HR-ToF-AMS) (Canagaratna, M. R. et al., 2007). Positive matrix factorization (PMF) was applied to the unified high resolution mass spectra organic species with NO+ and NO2+ ions.

RESULTS AND CONCLUSION

PMF analysis of the high-resolution organic mass spectra together with NO+ and NO2+ ions identified three organic and one inorganic factor: HOA, SVOOA, LVOOA and nitrate inorganic aerosol (NIA). The NOx family ions were assigned to different PMF factors due to the different physicochemical properties of nitrate components. As a consequence, one inorganic PMF factor (NIA), which is dominated by NO+ and NO2+ ions, is primarily recognized as a NH4NO3 factor.

Besides the presence of NOx (NO+ and NO2+) ions in the NIA factor, we also noticed their presence among the organic factors, nearly 28% of NOx are found from SVOOA factor. The fact that NOx ions distribute between organic and inorganic PMF factors indicates that nitrate (in the form of functional group) has both organic and inorganic chemical forms. Based on this observation, we can estimate the mass concentrations of nitrate in different chemical forms.

The average mass concentrations are 0.04 μg m−3 and 0.08 μg m−3 for organic and inorganic nitrate, respectively, with the organic nitrate accounting for 33.3% of the total nitrate mass. For organic nitrate aerosol, 74.4% of mass was assigned in SVOOA, suggesting that it is semi-volatile in nature, whilst we also observed 24.3% of organic nitrate in LVOOA and 1.3% in HOA. Its mass appears to originate from the south to west, where residential and forest areas are primarily located.

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A new direct inhalation exposure method for investigating combustion emission induced adverse health effects in mice

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Keywords: Inhalation exposure, combustion emissions, toxicity, particulate matter

INTRODUCTION

Currently, all the methods using filter collected PM in toxicological settings contain several confounding factors. In addition, potential toxicological effects of the gas phase are lost during sample collection. Thus, it is obvious that physicochemical properties of particles and concomitant toxicological responses are different to those from total emissions. Therefore, there is an urgent need for experimental animal studies based on direct exposure to the emissions and combining the health related toxicological responses and physicochemical characterization of the emissions. To overcome the limitations of the traditional sample collection and exposure methods, we have applied a novel online animal exposure system for the emission research.

METHODS

Pathogen-free male C57Bl/6J mice 8- to 9 week old, were exposed to diesel engine to emissions for 2h at different dilution ratios (DR; Low: 1:96; Medium: 1:50; High: 1:22) or to clean air as a negative control (Figure 1). At the exposure, the mice were placed into a monitored inhalation exposure unit (TSE-Systems, Bad Homburg, Germany). The diluted emission aerosol was led into the whole body exposure chamber. Simultaneously, air-liquid interface exposure system was tested in vitro.

Bronchoalveolar lavage fluid was collected for the measurements of inflammatory, cytotoxicity and genotoxicity markers at 4 h and 24 h after the exposure.

CONCLUSIONS

We showed in our pilot study that the parallel use of new direct inhalation exposure method and air-liquid interface exposure of the cells was applicable in combustion emission studies. We measured dose dependent increase in genotoxic activity in the pulmonary cells of mice after the exposure (Figure 2). However, due to short exposure time, no signs of inflammatory activity or cytotoxicity were observed.

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How to avoid particle–particle contacts between deposited silver nanoparticles?

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Keywords: silver nanoparticle, Liquid Flame Spray (LFS), localized surface plasmon resonance

INTRODUCTION
The optical properties of silver nanoparticles are dominated by the localized surface plasmon resonances. The wavelength of the plasmon resonance depends on the dielectric environment, particle size and shape. Applications for plasmonic materials include biosensors, solar cells and colored coatings.

Aerosol flame synthesis is a fast and a scalable process, and the generated particles can be collected on a desired material directly from the gas phase. However, during the collection process, unwanted contacts between individual particles arise, especially when the particle coverage on the substrate increases (Harra et al., 2012). These contacts effectively change the shape of the particles and, thus, the plasmon resonance band broadens significantly. In order to avoid this, silver particles can be, for example, encapsulated with a dielectric shell structure or embedded in a dielectric environment (Zdanowicz et al., 2013, 2014). In this study, we demonstrate an aerosol synthesis and deposition method that leads to spherical and well dispersed silver nanoparticles without additional dielectric material.

METHODS
Silver nanoparticles were synthesized with a flame synthesis process called Liquid Flame Spray (LFS, see e.g. Haapanen et al., 2014), using silver nitrate precursor. After the flame, the generated particles passed through a tubular flow channel. At the end of the flow channel, the particles were collected on a glass substrate at a temperature of a few hundred Celsius degrees. The synthesized particles were characterized in the aerosol phase and at the glass substrate with a scanning mobility particle sizer (SMPS) and a scanning electron microscope (SEM), respectively. The optical extinction spectra of the samples were measured with a UV-VIS spectrophotometer.

RESULTS AND DISCUSSION
Figure 1 shows an SEM micrograph of the collected silver nanoparticles on a glass substrate. The particles are spherical and well dispersed. As seen from the particle number size distributions in the insert, the particle size increases from 30 nm to over 40 nm during the collection process. This suggests that the particles coagulate and sinter on the substrate due to the elevated temperature. Reference samples collected at a lower temperature contained silver agglomerates and partially sintered particles.

The color of the prepared samples was yellow, typical to nanosilver, and the optical extinction spectra showed a plasmon resonance band near a wavelength of 400 nm. The samples collected at a lower temperature were grayish due to an additional extinction at longer wavelengths.

Figure 1. An SEM micrograph of spherical and well dispersed silver nanoparticles on a glass substrate. The insert shows particle number size distributions measured with an SMPS and calculated from the SEM micrograph.

ACKNOWLEDGEMENTS
J. Harra acknowledges TUT’s graduate school for financial support.

REFERENCES

Seasonal variation of aerosol chemical composition in the boreal forest

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Keywords: Aerosol chemical composition, seasonal variation.

INTRODUCTION
Aerosol chemical composition affects the physical and chemical properties of aerosols, such as optical properties and hygroscopicity. Knowledge of these properties is crucial when determining the climate effects of different aerosols. The aim of this study is to explore the seasonal variability of different chemical species in sub-micron aerosol particles in Hyytiälä, Finland.

METHODS
SMEAR II (Hari and Kulmala, 2005) is a boreal research site for measuring ecosystem–atmosphere relations. It is located in Hyytiälä, Southern Finland, where duration, chemical composition and ambient concentrations of aerosol loadings vary a lot depending on the wind directions and trajectories. To understand the natural seasonal variation of aerosol composition better, long time series are needed. Therefore Aerodyne Aerosol Chemical Speciation Monitor, ACSM, (Ng et al., 2011) has been continuously measuring chemical composition of refractory aerosols in SMEAR II since early spring of 2012.

The definitions of thermal seasons are used when dividing the data into spring, summer, autumn and winter.

RESULTS AND CONCLUSIONS
The prevalent role of organics can be seen in Fig. 1, where during summer the amount of organics compared to the whole mass concentration measured is 75%. During winter the number has decreased to 48%, whereas the percentage of sulfates has increased from 14% to 33%. The role of nitrates in the total mass concentration is between 4% and 8% showing the highest percentage during the winter. Ammonium does not differ from these other inorganic compounds, as the highest share of the total concentration is measured to be 11% at winter time and 7% at summer time. The amount of chlorides is usually below 1%.

Even though the temperatures during thermal spring and autumn are approximately the same, their pie charts in Fig. 1 are totally different. This could be explainable by the trend of the temperature, which is rising during spring and decreasing during autumn and its effects on the ecosystem. Therefore organics are the most dominant compounds during spring and summer. The higher amount of inorganics during autumn and winter is explainable by increased amount of anthropogenic combustion (Hewitt and Jackson, 2009) and decreased biogenic activity.

Figure 1. Percentages of different chemical species in the total refractory aerosol mass concentration in rural environment. Organic compounds appear as green, sulfates as red, nitrates as blue, ammonium as yellow and chlorides as purple. The data is from 20.4.2012 – 8.10.2014.

REFERENCES
The effect of hydration on particle formation rates in the sulfuric acid/amine system derived from quantum chemistry

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Keywords: sulfuric acid, amine, water, particle formation

INTRODUCTION
Atmospheric new particle formation generally involves sulfuric acid and water. These alone can, however, not explain observed formation rates. A substance known to enhance formation rates is ammonia, though insufficiently to explain observed rates. Amines, however, could explain the elevated formation rates are amines. Especially dimethyl-amine (DMA) has been found to be involved in particle formation events (Mäkelä et al., 2001).

We present a study on the effects of hydration on particle formation based on quantum chemistry calculations of clusters formed by sulfuric with ammonia, DMA, and water.

METHODS
Electronic structure calculations were performed on the first five hydrates of clusters containing up to four sulfuric acid and up to three ammonia or DMA molecules. Collision, and evaporation coefficients were derived from kinetic gas theory and equilibrium conditions, respectively. These were used to simulate all cluster interconversion processes between the calculated clusters, using values averaged over hydrate distributions. Particle formation rate was obtained as formation rate of clusters outside the system assumed to be stable.

CONCLUSIONS
Obtained free energies of cluster formation suggest clusters of a few sulphuric acid molecules to be hydrated by three to four water molecules under most conditions (Henschel et al. 2014). Base molecules in the clusters generally lower hydration, with DMA having a considerably stronger effect.

The effect of hydration on particle formation rates in the ammonia-containing systems is depicted in Figure 1. As can be seen, the effect can span a few orders of magnitude in either direction. The effect depends strongly not only on ammonia concentration and relative humidity as demonstrated, but varies also strongly with temperature and sulphuric acid concentration. For very high ammonia concentration, however, the system becomes similar to the sulphuric acid/DMA system, which under most conditions shows a slight increase (less than one order of magnitude) in particle formation rate with increasing relative humidity (Figure 2).

ACKNOWLEDGEMENTS
We thank CSC-IT Center for Science, Espoo, Finland, for computing time, and ERC StG 257360 MOCAPAF, and the Academy of Finland (Center of Excellence program project #272041, LASTU program project #135054) for funding.

REFERENCES
Online mass spectrometric composition analysis of particulate matter in mines

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Keywords: particulate matter, aerosol mass spectrometry, chemical composition, mining

INTRODUCTION
Particulate matter (PM) from mining operations, engines and ore processing may have adverse effects on the health and well-being of workers and of population living nearby. In this study, comprehensive measurement setups were used to characterize particulate air pollution in mines. The most advanced instruments deployed in the study were based on the mass spectrometry. Two aerosol mass spectrometer types were used to analyze sub-micrometer aerosol composition on real-time basis. The measurements taken are unique, representing the first ever collection of real-time and detailed, source-specific information on particle chemical composition in Finnish mines.

METHODS
The locations of the study which was carried out during spring 2014 included an underground mine and an open-pit mine. This presentation focuses on online composition measurements with two aerosol spectrometers. The TOF-ACSM (Aerodyne Time-of-Flight Aerosol Speciation Monitor) was used during several weeks in both locations. The instrument analyses chemical composition of non-refractory components of sub-micrometer aerosol. Parallel with the TOF-ACSM, soot, refractory component of aerosol, was measured as black carbon equivalent concentrations with the Multi-Angle Absorption Photometer (Thermo 5012 MAAP). The other aerosol mass spectrometer used in the study was the Soot Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research Inc.). The SP-AMS is even more advanced instrument than the TOF-ACSM as it can analyse also refractory components of aerosol (soot, metals) using laser vaporization of particles.

RESULTS
In the underground mine measurements were carried out 500 m underground. Composition of sub-micrometer particles was quite similar over most of the time. Major components were organic carbon and black carbon, both expected to be constituents of emissions from diesel engines. The frequently found short high concentration peaks of inorganic ions were most likely originating from blasting. The SP-AMS was short time used to measure the composition of PM in the exhaust air of the ventilation system (70 m3/s). It was found that particles experience quick growth by saturated water vapour in the exhaust channel, and the interstitial sub-micrometer particles analysed by the SP-AMS do not represent the composition measured with the TOF-ACSM at the – 500 m level. In the open-pit mining area the measurements were done a few hundred meters from the pit. The TOF-ACSM was measuring over six weeks, but the SP-AMS was available only for a short time. The polluted air could be measured only when the wind direction was favouring the transport of pollutants from the open-pit or from the passing vehicles. Vehicular diesel engine emissions measured using the aerosol mass spectrometers occurred as short-duration plumes simultaneously with mineral dust plumes from the ground surface (detected with other instruments). Thus the plume was a mixture of engine emissions and mineral dust, different sources representing different particle size ranges. As in the underground mine, the blasting made up short-time plumes where inorganic ions dominated the composition.

CONCLUSIONS
The study shows that advanced aerosol measurement technology is well suited for operation in the harsh environmental conditions in mines. The results reveal the major sources of particulate matter in mines, and help in the development of better control systems and in assessing health risks.

ACKNOWLEDGEMENTS
The presentation is based on the HIME project funded by the Finnish Funding Agency for Technology and Innovation (TEKES) in the Green Mining programme.
Current best accuracy of particle number concentration measurements


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Keywords: Calibration, comparison, particle number concentration, traceability

INTRODUCTION

Reliable and accurate particle number concentration measurements are only achieved using calibrated instruments traceable to the aerosol electrometer (AE). A number of national metrology institutes and expert laboratories provide traceable calibrations, but the metrological framework is incomplete because the equivalence of such calibrations has not been investigated. In this paper we present results of two world-wide inter-laboratory comparisons involving AEs and condensation particle counters (CPC) (EURAMET, 06/2014; EURAMET, 11/2014; Högström et al., 2014).

MEASUREMENTS

Measurements were performed by sampling particles from a common aerosol source with a range of particle materials (soot, silver, oil, salt), sizes (6 – 200 nm) and concentrations (100 – 20 000 cm−3). Figures 1 and 2 show examples of results.

CONCLUSIONS

Results show that the best achievable accuracy using calibrated CPCs is currently ±10 % even though the AEs agree within ±5 %. As an outcome, a solid metrological basis for number concentration measurements worldwide has been established.

ACKNOWLEDGEMENTS

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EURAMET (06/2014) project number 1244 – Comparison of aerosol electrometers.
EURAMET (11/2014) project number 1282 – Comparison of condensation particle counters.
HYGROSCOPIC PROPERTIES OF AMBIENT AEROSOLS DURING NEW PARTICLE FORMATION EVENTS

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Keywords: NEW PARTICLE FORMATION, HYGROSCOPICITY

INTRODUCTION

New particle formation (NPF) and subsequent growth has been observed to occur almost everywhere throughout the atmosphere. Measuring the hygroscopic properties of aerosol particles, especially those of nucleation and Aitken mode particles during NPF event, provides indirect information about the chemical composition of the particles and physical properties of compounds in these particles.

METHODS

The measurements were performed during 6 April to 3 June at SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations II), located in Hyytiälä, Southern Finland. In this study, we conducted the measurements of hygroscopicity for nucleation, Aitken and accumulation mode particles (30 nm, 60 nm 100 nm and 145 nm) using a Hygroscopic Tandem Differential Mobility Analyzer (HTDMA). (Hong et al., 2014). A High-Resolution Aerosol Mass Spectrometer (HR-AMS) was used to determine the chemical composition of aerosol particles during the experimental period.

Table 1. HGF and density of all compounds used in the ZSR calculation (Gysel et al., 2007).

<table>
<thead>
<tr>
<th>Density (kg m⁻³)</th>
<th>GF (90%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>1769</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>1780</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>1720</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>1830</td>
</tr>
<tr>
<td>Organic</td>
<td>1400</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Time series of predicted growth factor based on chemical composition data using the ZSR mixing rule are plotted in the upper panel of Fig. 1.

In the lower panel of Fig. 1, a comparison between HTDMA-measured growth factor and AMS-predicted growth factor was made for event days, non-event days and undefined days. A general pattern was that the correlation between the AMS-derived HGF and HTDMA-measured HGF increases with an increasing particle sizes for all the days, implying that the HR-AMS can reflect the chemical composition of particles larger than 50nm quite well during the defined days. The deviation of the fitting line from the 1:1 line can be explained by two possible reasons that organics in different size particles have different HGF due to different origins (e. g. aging), or smaller particles contain a bigger organic fraction than larger particles.

ACKNOWLEDGEMENTS

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REFERENCES


A combined approach for virtual reality model simulation to calculate the personal inhaled deposited dose of aerosol particles indoors and outdoors

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Keywords: particulate matter, particle number, health risk, indoor aerosol model

INTRODUCTION

Exposure to harmful particulate matter (PM) could occur anywhere. Since people spend most of their time indoors, the exposure indoors tends to dominate the 24-hour personal exposure. Moreover, higher PM concentrations due to indoor sources and tightness of indoor environments may substantially add to the outdoor originating exposures.

METHODS

Indoor aerosol modelling (IAM) can be used as an alternative method to experimental methods in exposure and health effects studies because empirical and real-time assessment of human exposure is often impossible. We, therefore, developed a simple approach in combining available aerosol-based modeling techniques to evaluate the real-time exposure and respiratory tract deposited dose based on particle size (Hussein et al., 2014).

Our simple approach consists of outdoor aerosol data base (either measured, modelled, or forecasted), IAM simulations, time-activity pattern data-base, physical-chemical properties of inhaled aerosols, and semi-empirical deposition fraction of aerosols in the respiratory tract (Figure 1). The combination of these modelling and empirical techniques allow the characterization of regional deposited dose in any metric: particle mass, particle number, and surface area.

CONCLUSIONS

To support the proposed approach, there is a great need for detailed information about: (1) indoor environment (geometry, conditioning, etc.), (2) physical-chemical properties, (3) emission rates of aerosol particle produced indoors, (4) long-term of size-resolved outdoor aerosol data-base, (5) time-activity patterns of urban population, and (6) aerosol deposited fraction in human lungs for different age groups, gender, and health conditions.

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REFERENCES

Aerosol direct radiative effect efficiency, aerosol optical properties and surface albedo - comparison between simulations of models and results derived with observations

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Keywords: aerosols, radiation, measurements, simulations

INTRODUCTION

In this study, models from the AeroCom Phase II experiment will be validated with observations. The parameters of the study are Aerosol Optical Depth (AOD), Ångström exponent (AE), Absorption AOD (AAOD), Single Scattering Albedo (SSA), surface albedo and the Aerosol Direct Radiative Effect Efficiency (ADREE). ADREE is defined as the difference between solar flux with and without aerosols normalized by AOD. Solar fluxes are collected from Solar Radiation Network (SolRadNet, http://solrad-net.gsfc.nasa.gov/) and Baseline Surface Radiation Network (BSRN, http://www.bsrn.awi.de). The Aerosol Robotic Network (AERONET) (http://aeronet.gsfc.nasa.gov/) provides AOD, AAOD, SSA and surface albedo.

METHODS

The observational based ADREE is calculated with a nonlinear regression method using solar flux and AOD observations. The other parameters (AOD, AAOD, SSA, AE and albedo) can be compared for all the available AERONET stations (in addition of the comparison for the same stations as in the ADREE estimates). Furthermore, libRadtran (library for radiative transfer, http://www.libradtran.org)-code is implemented to provide ADREE based on the AERONET observations, providing ADREE for hundreds of stations, giving an additional source of ADREE.

CONCLUSIONS

So far we have all the results (ADREE, AOD, AE, AAOD, SSA and albedo) for four models. ADREE is provided already from seven models. Some of these seven models probably update their version during the study. Fig. 1 shows ADREES for models compared with the regression based ADREE. The preliminary results indicate that: 1) already these four models provide significantly different global annual averaged ADREES, 2) the regression method has its limitations, but still is a valuable reference for model based ADREES, 3) observational based aerosol optical properties are crucial for explaining the difference in ADREE and their data analysis, including e.g. additional criteria to limiting the data, affect on the analysis significantly. So far the results indicate that SSA is overestimated by the models, thus aerosol absorption is underestimated (not shown). The goal is to finalize the study during 2015. Moreover, in the near future, the analysis can be extended with the top of the atmosphere observations, providing more information into the topic.

Figure 1. ADREEs from the models (CAM4-Oslo, GMI, HadGEM2 and Oslo CTM2) compared with observational based ADREES, each of the marks are seasonal (Dec-Feb, Mar-May, Jun-Aug, Sep-Nov) averaged values for year 2006. CAM4-Oslo in averaged over few years, not only 2006. Units in Wm$^{-2}$.

ACKNOWLEDGEMENTS

The authors thank ground-based and satellite remote sensing groups, especially AERONET, BSRN and SolRadNet.
Modeling the Detection of Highly Oxidized Cyclohexene Ozonolysis Products Using Nitrate-Based Chemical Ionization

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Keywords: ELVOC, cyclohexene ozonolysis, nitrate CIMS

INTRODUCTION

Recent laboratory and field experiments (Ehn et al., 2014) indicate that the autoxidation of alkenes may play a significant role in the formation and growth of secondary organic aerosol particles. This autoxidation process is initiated by an oxidant such as OH or O₃, and very likely propagated by hydrogen shift and subsequent oxygen addition reactions of peroxycarboxy intermediates. Uni- and bimolecular termination reactions lead to closed-shell products with multiple peroxy and carbonyl functional groups.

Computational and laboratory studies (Rissanen et al., 2014) show that cyclohexene ozonolysis produces Extremely Low Volatility Organic Compounds (ELVOCs) with high O:C ratios. In this study the Gibbs free energies of four representative ELVOC compounds and their nitrate clusters were calculated using quantum chemical methods, with extensive configurational sampling. The studied ELVOC candidates contain both peroxy and carbonyl functional groups, and have the molecular formulae C₆H₆O₂, C₈H₁₀O₇, C₈H₉O₈, and C₉H₈O₉.

METHODS

We have developed and tested a configurational sampling approach (Rissanen et al., 2014) for studying hydrogen shift reactions in peroxycarboxylates, and applied it to the cyclohexene ozonolysis system. Force-field methods are first used to explore all possible combinations of torsional angles, yielding a set of up to thousands of distinct trial structures for each system. This set is narrowed down by subsequent density functional theory calculations of increasing sophistication. The energy of the lowest-lying conformers are then finally evaluated using the coupled cluster method DLPNO-CCSD(T).

The computed free energies are used to explain the results of a laboratory measurement where highly oxidized cyclohexene ozonolysis products were detected using a chemical ionization setup with nitric acid – nitrate clusters as charger ions. The interactions between molecules and clusters are simulated with Atmospheric Cluster Dynamics Code (ACDC).

From the free energies we calculated the formation free energies of the clusters of our representative ELVOCs with nitrate ions. The binding of the ELVOCs to nitrate ions becomes stronger as the number of hydrogen-bonding OOH groups increases, and at least two OOH groups are required for the cluster to be more stable than HNO₃(NO₃)₂. The C₆H₆O₆ molecule has a double bond in the carbon chain, which may lead to ring strain and thus less favorable cluster structures.

The calculations are in agreement with experimental measurements that show no significant signal for C₆H₆O₃(NO₃)₂. The measurements show that C₆H₆O₄(NO₃)₃, which has the lowest free energy, also has the largest signal. The C₆H₆O₇(NO₃)₃ (Figure 1) and C₆H₆O₉(NO₃)₃ signals are both less than half of the C₆H₆O₆(NO₃)₃ signal.

The simulations indicate that the relative ion cluster signals obtained in a chemical ionization measurement setup strongly depend on the nitric acid concentration in the instrument. It is also probable that the observed signal for C₆H₆O₈ corresponds to a different structure with the same chemical formula.

ACKNOWLEDGEMENTS

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REFERENCES

A new ice nuclei counter SPIN: characterization and comparison to LACIS

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Keywords: ice nuclei counter, heterogeneous ice nucleation, mineral dust

INTRODUCTION

Aerosol particles known as ice nuclei (IN) play an important role in the atmosphere in a number of processes related to cloud formation and cloud microphysics. Despite the progress within ice nucleation research during the past decade, much is still unknown. There is a particular need for data on atmospheric IN number concentrations from observations, as only a small number of these observations exist, while they would provide valuable input for atmospheric modelling (DeMott et al., 2010). In situ measurements with portable IN counters are an important way to gain knowledge in this field.

METHODS AND RESULTS

The Spectrometer for Ice Nuclei (SPIN) is a new commercially available portable IN counter manufactured by Droplet Measurement Technologies, Inc. SPIN is a continuous flow diffusion chamber following the operation principle of the airborne CFDC IN counter (Rogers et al., 2001). The main difference lies in parallel plate geometry (in contrast to the cylindrical chamber of the CFDC), adapted from the design of the Portable Ice Nucleation Chamber (PINC) (Chou et al., 2011) and Zurich Ice Nucleation Chamber (ZINC) (Stetzer et al., 2008). The aerosol sample flows through a chamber where a supersaturation of water vapor with respect to ice is obtained by keeping two ice covered walls at different temperatures below 0°C (see Figure 1). The aerosol sample is then exposed to an isothermal, separately temperature-controlled evaporation section where the unfrozen droplets evaporate in contrast to the ice crystals before particle detection with a linear depolarisation optical particle counter (OPC).

With SPIN, it is possible to investigate heterogeneous ice nucleation under sub- and supersaturated conditions with respect to water, i.e. in both deposition nucleation and immersion freezing modes. We have tested the SPIN chamber with well characterized mineral dust and biological ice nuclei such as illite and SNOMAX™, as well as investigated the homogeneous freezing of ammonium sulphate particles. Here we present exemplary results of these studies and a comparison to immersion freezing results obtained with the Leipzig Aerosol Cloud Interaction Simulator (LACIS) (Hartmann et al., 2011).

ACKNOWLEDGEMENTS

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REFERENCES

Gas Phase Advanced Oxidation model development and verification using actinometry

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Keywords: Air purification, UV, Ozone, Hydrogen Sulfide

In Gas Phase Advanced Oxidation (GPAO) hydroxyl radicals (OH⁻) are used to oxidize and remove pollutants from industrial exhaust (Johnson et al., 2014). OH⁻ are generated from ozone photolysis, as shown in reactions 1 and 2.

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \quad (1)
\]

\[
\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}⁻ \quad (2)
\]

Typical oxidation products of common pollutants show lower vapour pressure and higher water solubility than the pollutant itself. Products will therefore condense upon pre-existing particles or initiate nucleation of new particles which are removed later in the treatment.

Since hydroxyl radicals are the initiators of almost all oxidation reactions taking place in GPAO it is necessary to optimize their production in order to increase the efficiency of the GPAO treatment. Reaction 1 is the limiting reaction that leads to OH⁻ and it depends on UV intensity, geometry of the lamp setup, material properties etc.

A kinetic Cantera model of a series of perfectly stirred reactors was used to describe the laboratory GPAO prototype and to determine its rate of OH⁻ production. The model consists of 3 ideal gas reactors. In the first reactor polluted air is mixed with ozone, in the second the mixture is exposed to UV light while the third is an empty space where the radical reactions continue until the end of simulation. The model consists of 30 HOₓ and Oₓ reactions, and takes thermodynamic properties of all species into account. The model does not however include wall reactions or particle formation but is strictly a gas phase kinetic model. The model output is based on experimental data of ozone removal in the prototype under varying experimental conditions, i.e. volumetric flow, ozone concentration, and the number of UV lamps.

Figure 1 shows the modelled photolysis rates of ozone as a function of lamp number. It is seen that OH⁻ production is independent of flow rate and ozone concentration while changing number of lamps shows a big impact on the photolysis rate. The results also indicate that OH⁻ production scales almost linearly with the number of lamps. The photolysis rate/lamp is estimated to be $2.98 \times 10^{-9}$ mol/s/lamps. Which is between 100 and 10,000 times higher than tropospheric ground level values depending on the solar zenith angle and the ozone column density (Bahe et al., 1976). With the photolysis rate determined, it is possible to model the removal of pollutant species and compare the simulations to experimental data. Hydrogen sulfide was chosen as the pollutant because of its simple molecular structure and its obnoxious smell which makes it a problematic pollutant for many industries.

A study of the stable oxidation products from H₂S was conducted using online Fourier Transformed Infrared spectroscopy (FTIR). Quantitative and qualitative measurements identified SO₂ as a stable oxidation product. Further treatment showed a decrease in sulfur dioxide concentration while producing a large amount of particles which indicates further oxidation to sulfuric acid.

We will present the basic Cantera model; the actinometry and H₂S experiments as well as the comparison between the model and experimental results.

REFERENCES


Modeling the Detection of Organic and Inorganic Compounds Using Iodide-based Chemical Ionization

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Keywords: Chemical ionization, mass spectrometry, iodine, clusters, detection limit

INTRODUCTION

Chemical ionization mass spectrometry (CIMS) using iodide-molecule adduct formation has become an important approach for quantifying carboxylic acids, HNO₂ species, and halogen molecules in the atmosphere (Lee, et al., 2014). Iodide-based mass spectrometry may also be useful in studying recently detected ELVOC (extremely low volatility organic compounds) molecules.

In this study, the binding enthalpies of a number of organic and inorganic compounds - (ranging from Cl₂ to complex products formed in isoprene oxidation) to iodide ions were calculated using quantum chemical methods. These were then compared to the detection limits of the University of Washington iodide CIMS for these molecules. The results are shown in Figure 1.

METHODS

The molecules were built using the Spartan ’14 program. All possible conformers from different combinations of torsional angles were generated and optimized to obtain minimum energy geometries. Molecular energies were calculated using the Gaussian 09 program (Frisch, et al., 2010) with the PBE density functional and the aug-cc-pVTZ-PP basis set. Binding enthalpies of molecule-I clusters were calculated, and compared to the corresponding detection limits of the CIMS instrument.

CONCLUSIONS

Binding enthalpies calculated with relatively simple quantum chemical methods predict the detection efficiency of molecules with an iodide-based CIMS instrument remarkably well. This indicates that quantum chemical data can be used to convert CIMS signals into order-of-magnitude estimates of the concentrations of neutral precursor species. This may be useful in future studies of e.g. ELVOC molecules. Chlorine and bromine had the highest binding energies to iodide, as they reacted with it to form a covalently bound I-X-X- molecular ion (where X = Cl or Br). Consequently, these molecules were better detected by the instrument than any other studied molecule. Peroxyacetic acid had the lowest binding energy to iodide, and thus the highest detection limit among the studied molecules. This is likely due to the efficient formation of an intramolecular hydrogen bond in the free peroxyacetic acid molecule, which decreases the favorability of bimolecular bonding reactions.

In addition to calculating the binding enthalpies of molecule-iodide clusters, we also investigated the effect of humidity on the detection efficiency of HNO₂ (with x = 2,3,4) and halogen molecules Cl₂ and Br₂. The binding energy of nitrous acid HNO₂ and peroxyacetic acid HNO₄ to iodide decreased significantly when a water molecule was added to the system. This probably explains the observed decrease in their detection efficiencies as a function of humidity. For HNO₃, Cl₂ and Br₂, the thermodynamic effect of hydration on the binding enthalpies was minor. The observed increase in the detection efficiencies of these species as a function of humidity is thus likely due to the kinetic stabilization associated with the extra vibrational degrees of freedom.

ACKNOWLEDGEMENTS

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CCN activation and aerosol hygroscopicity during autumn 2011 in Po Valley, Italy

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Keywords: aerosol, cloud condensation nuclei, hygroscopicity

INTRODUCTION

An aerosol particle's response to a change in humidity is a function of its size and chemical composition. Soluble particles take on water and grow with increasing humidity. Aerosol particles become climatically important if they are able to grow to sizes of 50 nm and larger. Particles in this size range can act as cloud condensation nuclei (CCN) and therefore may contribute to the indirect aerosol effect (Twomey, 1991).

Once particles grow to a size where they can become CCN, their ability to activate into cloud droplets depends on their chemical composition, particle number concentration, and the water supersaturation of the surrounding air parcel. Because both aerosols and clouds have a substantial influence on the climate, the fundamental purpose in looking at aerosol-cloud interactions and particle hygroscopicity is to find a relation between the activating aerosol particle and the resulting cloud droplet population.

METHODS

A data set of size-resolved CCN concentrations, measured by a DMT-CCNc (Cloud Condensation nuclei counter, Roberts & Nenes, 2005) from the San Pietro Capofigline measurement station in Northern Italy (44°39'N, 11°37'E, 10 m a.s.l.) was analyzed for the time period of 15 days (15.11.2011 - 29.11.2011). San Pietro Capofigline (SPC) station is located about 30 km northeast from the city of Bologna, in the Po Valley. The station itself is in a sparsely inhabited area, but high levels of pollutants are observed in this region due to its geographical location.

κ-Köhler-theory was used to calculate the hygroscopicity parameter κ (Petters & Kreidenweis, 2007) for the ambient aerosol using the CCN data for three different supersaturations (SS=0.1, 0.2 and 0.4%) were 0.12, 0.21 and 0.35, respectively. The corresponding critical diameters (Dc) were 158, 120 and 89 nm, respectively.

CONCLUSIONS

Average CCNc-derived κ values during the intensive campaign for the three different supersaturations (SS=0.1, 0.2 and 0.4%) were 0.12, 0.21 and 0.35, respectively. The corresponding critical diameters (Dc) were 158, 120 and 89 nm, respectively.

In future work, we will compare our present results with the hygroscopicity values derived from subsaturated water vapour regime data (Hygroscopicity Tandem Differential Mobility Analyzer, HTDMA) and on the other κ derived from the chemical composition data (High Resolution Time-of-Flight Aerosol Mass Spectrometer, HR-ToF-AMS).

ACKNOWLEDGEMENTS

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REFERENCES

Lung diagnosis by recovery of inhaled nanoparticles: evaluation of the Airspace Dimension Test within the Swedish CArdioPulmonary bioImage Study

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Keywords: lung deposition, nanoparticles, COPD, health

INTRODUCTION

The Swedish CardioPulmonary bioImage Study, (SCAPIS) is an extensive scientific project, carried out to create a national database with detailed medical information on a total of 30 000 individuals to identify risk markers for cardiovascular and lung disease.

The Airspace Dimension Test (ADT) is a unique and recently developed technique aiming at assessing pulmonary airway dimensions and possible pathological changes of the lungs such as pulmonary emphysema by measurement of lung deposition of nanoparticles in a single breath procedure (Jakobsson et al., 2014). The aim of this project is to validate ADT by measurements on the group of subjects participating in the SCAPIS cohort.

METHODS

The subjects participating in the SCAPIS project are going through a thorough medical examination including complete spirometry, DLCO, and computed x-ray tomography. The data from different examinations provide an extensive characterisation of the subjects lung function and anatomical lung features.

The ADT technique measures the recovery of nanoparticles after a single breath vital capacity manoeuvre. A monodisperse aerosol of PSL nanospheres, with a concentration comparable to indoor ambient air, is inhaled and allowed to deposit by diffusion during a controlled breath holding time. The particle recovery is measured in a well-defined volume extracted from the exhaled air. Several tests with different breath holding times are performed on each subject.

The breath holding times were varied between 5-10 s, and in general two measurements were performed on every breath holding time on every subject. Individual differences in breathing pattern resulted in a spread of diffusion times from 6-16 s during the experiment.

Particles with a mobility diameter <300 nm deposits in the lungs almost exclusively by diffusion, and it is hypothesised that the measurements reflect properties such as average diffusion distances in the airspaces or available surface area in the lung tissue.

RESULTS

ADT Recovery 10 s

Figure 1: The distribution of ADT recovery at 10 s for 65 subjects.

It was found that measured particle recovery and diffusion time in the lungs correlated well with an exponential relation (on average Pearson r=0.988). This agrees with theory of diffusional particle deposition. It was also found that the data could be normalized to a diffusion time of 10 s, and thus subjects could be compared independent of individual breathing patterns. The average ADT recovery of a group of 65 subjects was 0.097±0.053 at 10 s diffusion time, 0.071±0.042 at 12 s diffusion time and 0.060±0.038 at 13 s diffusion time.

CONCLUSIONS

The results imply that it is possible to use a single ADT measurement to observe inter-subject differences and information associated with dimensions of the lungs. The data is likely to reflect mean diffusion lengths of the pulmonary region of the lung or surface area available for diffusion. The ADT technique may be the most accessible option to detect early emphysema, which is one of the most common diseases globally.

ACKNOWLEDGEMENTS

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Diffusion charger based monitoring of urban aerosols

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Keywords: urban air quality, diffusion charger, particle sensor

INTRODUCTION

The outdoor air quality monitoring has usually been based on particle mass measurements: PM₁₀ and PM₂.₅. However, the toxicity of nanoparticles has been linked to particle surface area (Oberdörster 2001; Waters et al. 2009) but this link has not yet been demonstrated for outdoor air particles.

To demonstrate the simplicity of measuring lung deposited surface area (Fissan et al. 2007) of outdoor air nanoparticles, diffusion charger based PPS-M sensors (Pegasor Oy) were used to monitor outdoor air quality in Helsinki Metropolitan area.

METHODS

The sensors were installed into measurement stations located in Malmi Ring road I (roadside), Kattilalaakso (residential) and into a mobile laboratory (Pirjola et al. 2004) (Helsinki city centre). The instrument setup varied between the sites. The detailed description of the measurement sites and instruments is given in Järvinen et al. (2014).

CONCLUSIONS

The PPS-M response to PM₂.₅ varied between the measurement sites and times as a result of different median particle sizes. The highest response was observed in the roadside measurement, where the particle size was the smallest, see Table 1. In conclusion, the sensor output weights smaller particle sizes than mass based measurements. For the roadside, the sensor output was found to be rather linear to NO and NO₂ concentrations, confirming that the particles measured by the PPS-M originated from traffic.

The PPS-M was found to produce highly linear response to the lung deposited surface area concentration (LDSA by NSAM) and to the condensation sink of outdoor aerosol (CS). The response to CS was almost constant in all of the measurement sites.

Table 1. The PPS-M response fA/(reference unit) for measured air quality factors, see Järvinen et al. (2014). Residential area has been divided into low (L) and high (H) PM₂.₅ background periods.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Residential</th>
<th>Roadside</th>
<th>Mobile</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>PM₂.₅ (μg/ m³)</td>
<td>13</td>
<td>7.0</td>
<td>30</td>
</tr>
<tr>
<td>NO (μg/ m³)</td>
<td>9.8</td>
<td>240</td>
<td>4.8</td>
</tr>
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<td>NO₂ (μg/ m³)</td>
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<td>7.1</td>
</tr>
<tr>
<td>N (1/cm³)</td>
<td>-</td>
<td>-</td>
<td>0.0044</td>
</tr>
<tr>
<td>CS (1/s)</td>
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<td>1.0x10⁴</td>
<td>1.0x10⁴</td>
</tr>
<tr>
<td>LDSA (μm²/cm³)</td>
<td>-</td>
<td>6</td>
<td>4.5</td>
</tr>
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</table>

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REFERENCES

Investigating the regional scale impacts of amine-sulphuric acid nucleation

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Keywords: Amines, chemical transport model, nucleation

INTRODUCTION

Nucleation is an important contributor to the atmospheric particle number concentration, and consequently a detailed understanding of the nucleation process and the compounds involved is essential for correct predictions by large scale models. Sulphuric acid is a central component for atmospheric new particle formation, but it is also known that other species, such as ammonia and amines, are required to account for the observed nucleation rates. Since both ammonia and amines are base compounds, they can act to stabilize the sulphuric acid containing clusters and thus enhance nucleation rates.

Amines are emitted to the atmosphere from a multitude of sources, both anthropogenic and natural, making amines quite ubiquitous (Ge et al., 2011). Even though the atmospheric amine concentrations are notably smaller than that of ammonia, amines are, in general, stronger bases than ammonia. This enables amines to stabilize small clusters more effectively and therefore their role in atmospheric new particle formation cannot be ignored. Indeed, recent experimental results show that amines can enhance nucleation rates over thousand-fold compared to ammonia (Almeida et al., 2013).

METHODS & CONCLUSIONS

PMCAMx-UF is a three-dimensional regional chemical transport model that includes detailed aerosol microphysics and simulates both number and mass/composition size distributions (Jung et al., 2010). PMCAMx-UF uses the DMAN model by Jung et al. (2006) for the aerosol microphysics. Recently the condensation of organic species, as described by Patoulias et al. (2014), has been added to PMCAMx-UF. In the previously applied versions of PMCAMx-UF (e.g. Fountoukis et al. 2012, Ahlm et al. 2013), two nucleation pathways have been present in the model: binary sulphuric acid-water nucleation and the ternary ammonia-sulphuric acid-water nucleation.

For the present study we have updated PMCAMx-UF to include amines for the first time. As a central feature, the updated version now includes also the amine nucleation pathway in addition to the two aforementioned nucleation mechanisms. The treatment of amine nucleation that has been added to PMCAMx-UF is based on nucleation rate data produced by the Atmospheric Cluster Dynamics Code (McGrath et al., 2012), which utilizes state-of-the-art quantum chemistry results to calculate cluster evaporation rates. We will present results where the updated version of PMCAMx-UF is applied to the European domain.

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REFERENCES

Simple real-time effective density and quality monitor for nanoparticles

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Keywords: effective density, low pressure impactor, mobility analyzer

INTRODUCTION

Typically, nanoparticle size and morphology are properties that define the quality of the produced nanomaterial, and they are required to stay constant for long periods of time. These are usually measured using off-line methods, such as electron microscopy, or on-line aerosol instrumentation (Ristimäki et al, 2002). Both of these methods require additional data processing in order to gain the information needed to properly evaluate the quality of the produced nanomaterial.

Here, we introduce simplified version of the measurement device presented by Rostedt et al. (2009), which is capable of measuring both aerodynamic and mobility diameters of an aerosol particle size distribution as well as calculate the effective density and total number concentration with a time resolution of one second.

METHODS

The instrument’s functionality is based on characterization of the aerosol by different collection mechanisms and the subsequent current measurement of the charge carried by the particles. First the aerosol particles are unipolarly charged using a corona charger after which the flow is directed through a mobility analyzer, a low pressure slit impactor (Arffman et al, 2012) and a filter. From these three sections, the current is measured using an array of electrometers. A schematic view of the instrument is presented in Figure 1.

Aerosol flow

Charger

MA → I₁

Impactor → I₂ → da, db → ρeff

Filter → I₃

Low pressure

Figure 1. Flow chart of the instrument and the information which is obtained from the measurement. MA refers to the mobility analyzer.

The mobility analyzer is used to determine the mean mobility diameter \(d_b\) of the aerosol distribution by collecting a portion of the aerosol based on electrical mobility. The aerodynamic diameter \(d_a\) is obtained from the inertially collected portion of the aerosol distribution. Using these two characteristic diameters, the effective density can be calculated from the following equation,

\[
ρ_{\text{eff}} = ρ_0 \cdot \frac{C_c(d_a) \cdot d_a^2}{C_c(d_b) \cdot d_b^2}.
\] (1)

The remainder of the particle size distribution that penetrates the mobility analyzer and was not collected by the impactor is deposited into a filter, and thus the last part of the total current carried by the nanoparticles is measured. This can be used to quantify the total number concentration.

CONCLUSIONS

The instrument presented here is capable of measuring the effective density, the average mobility and aerodynamic diameters and total number concentration with a time resolution of one second. The simple construction and a current measurement based operation principle makes it a promising tool for on-line monitoring of nanomaterial synthesis.

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REFERENCES


GENERATION, CHARACTERIZATION AND SIZING OF NEUTRAL SUB-3 NM METAL CLUSTERS

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Keywords: NEUTRAL CLUSTER, NANOPARTICLES, CPC, PARTICLE GENERATION

INTRODUCTION

Neutral particle sizing in the nanometer size range usually relies on known particle charge equilibrium and measurement of the charged fraction of the particles. At sizes below 3 nm, this method becomes unusable due to the high particle diffusion losses and the low charging probabilities. In addition, the charging method generates ions overlapping with the smallest sample particles. Methods to size-resolve particles without charging are needed in the sub-3 nm sizes, and their characterization requires methods to generate neutral sub-3 nm particles. Therefore, the sub-3 nm metal cluster generation method and the sizing of these clusters with the Particle Size Magnifier (PSM (Vanhanen et al., 2011)) are the focus of this study.

METHODS

Small particles were generated with a hot wire generator (Peineke et al., 2006) by heating four different wires: palladium, molybdenum, tungsten and nickel chromium. Their chemical composition was measured with a high resolution mass spectrometer (Junninen et al., 2010). The PSM was calibrated with tungsten oxide to measure size distributions between 1 and 2.9 nm and the measured size distribution was compared to a distribution measured by a high resolution DMA and an electrometer.

CONCLUSIONS

We have developed methods to generate sub-3 nm metal clusters of known composition and characterized the chemical composition of the clusters. From different metals we selected tungsten and showed that the sizing range of the PSM can be extended up to 3 nm by increasing the saturator flow rate maximum to 2 lpm. By calibrating the PSM, we showed the agreement to DMA+electrometer combination, which was found to be good, suggesting that the PSM can measure sub-3 nm neutral size distributions when calibrated and operated soundly. Combination of sub-3 nm particle generation and measurement allows research on small cluster dynamics and other related phenomena.

ACKNOWLEDGEMENTS

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REFERENCES

Li4Ti5O12 nanoparticles synthesised with a modified flame spray pyrolysis

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Keywords: Flame synthesis, Nanoparticle, Energy storage, Characterisation

INTRODUCTION

Lithium titanium oxide (Li4Ti5O12, LTO) is recognized as a promising material for the negative electrode of Li-ion batteries as it is cheap and safe, and has an excellent cycle life (Du Pasquier et al., 2003). However, the major drawback of LTO is its low electronic conductivity. To overcome this problem the particle size can be reduced to the nanoscale increasing the specific surface area, and decreasing the diffusion lengths within particles and the local current density (Arico et al., 2005). For LTO an optimum size of about 17 nm has been reported (Kavan et al., 2003). However, the current method of solid-state chemical reaction typically produces LTO particles with a diameter of the order of 1 μm. Another solution is to use metal dopants, e.g. silver (Huang et al., 2006). Currently the doping is typically carried out in a separate process which increases the complexity and costs of the production.

METHODS

Here, pure and doped LTO nanoparticles are prepared in the gas phase with flame spray pyrolysis (FSP). It is a fast, dry, and single-stage process that enables the preparation of materials with high-purity (Mädler et al., 2002). The precursor solution used for the studies contained lithium acetyl acetonate and titanium isopropoxide in an organic solvent. The silver doping was performed by adding silver 2-ethyl hexanoic acid directly into the precursor solution. Finally, a vertical flow furnace was used to increase the high-temperature residence time and thus the crystallinity of the particles.

CONCLUSIONS

The resulting particles were found to be high-purity (99%), single crystalline nanoparticles with a primary particle size down to 10 nm. A uniform dopant distribution was observed in the doped LTO nanoparticles. The silver dopant nucleated independently and deposited on the surface of the LTO particles (Karhunen et al. 2011). When the nanoparticulate pure LTO was used as the negative electrode in a Li-ion half cell the specific capacity was found to match that of a commercial reference LTO during low current operation (0.2C). However, when high currents (10C) were applied the capacity increased on average by 6%. Furthermore, improvements of 3% and 19% were observed for the silver doped LTO nanoparticles for the low and high currents, respectively.

![Figure 1. Electrochemical behaviour of pure and doped Li4Ti5O12 nanoparticles](image-url)

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REFERENCES

The effect of biogenic volatile organic compounds on aging of compounds emitted from anthropogenic sources

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Keywords: α-pinene, Aging, Anthropogenic emission sources, Volatile organic compounds

INTRODUCTION

Large quantities of volatile organic compounds (VOCs) are emitted into the atmosphere from vegetation (estimated to be 4150 Tg (C) yr⁻¹) globally, and they are significant source of secondary organic aerosol (SOA) (Guenther et al., 1995). Besides biogenic sources many different anthropogenic sources are emitting VOCs (estimated to be 400 Tg (C) yr⁻¹) and particles into the atmosphere, as well (Atkinson & Arey, 2003). Due to the simultaneous emissions that both sources are emitting the importance of their study, not just separately but also as a mixture is evident.

In this study the effect of α-pinene on species emitted from diesel car engine and pellet burner were explored during their aging. To our knowledge this is the first time, when the real anthropogenic emission sources were used for this kind of aging studies. This will offer more realistic picture of the processes, which are taking place in the atmosphere.

METHODS

The experiments took place in a 29 m³ teflon chamber. The objective of the study was to clarify the effect of biogenic VOCs on aging of species emitted from anthropogenic sources. To understand the effect of α-pinene on species from anthropogenic sources, experiments with and without added α-pinene were carried out in the presence of O₃. HONO was used as OH source and it was added just before UV-lights (blacklight lamps centered at 365 nm with a half-width of 16 nm) were switched on and aging of the species started.

The monitoring of the species was carried out by aerosol mass spectrometer (SP-AMS, Aerodyne Inc., Billerica, MA) for particle-phase species, and by high-resolution proton transfer reaction mass spectrometer (PTR-TOF 8000, Ionicon Analytik, Innsbruck, Austria) for VOCs. Also O₃ and NOₓ concentrations were monitored during the experiments using a trace-level chemiluminescence NO-NO₂-NOₓ analyser (Thermo 42i-TL) and an UV photometric ozone analyzer (Thermo 49i). The particle size distribution in the chamber was monitored with a scanning mobility particle sizer (SMPS; TSI 3081 DMA 3775 CPC).

CONCLUSIONS

Lots of different species were found from gas-phase, such as many oxygenated and nitrogen-containing compounds, and many of them were identified with certain reliability. This study demonstrated that α-pinene seemed to have an effect on aging of nitrogen-containing VOCs emitted from anthropogenic sources.

In particle-phase, increasing nitrate fraction was observed to be characteristic only for pellet burner emission. AMS/SMPS comparison suggests that diesel particles were mostly black carbon and the presence of α-pinene mainly affected the increase of organic fraction. The formation of the nitrate fraction is still under study and open questions still remain, such as why pellet burner emission causes the increase of nitrate fraction but diesel engine emission does not and what is the composition of the increasing particle nitrate fraction.

O₃/NOₓ chemistry taking place in the chamber was mimicking well the chemistry occurring in the atmosphere. After the UV-lights were turned on the photostationary steady-state was reached in O₃/ NOₓ cycling and some O₃ was produced.

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REFERENCES


Nanoparticle emissions from modern gasoline fueled passenger cars

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Keywords: particle emissions, gasoline, soot, engine braking

INTRODUCTION

Vehicle technology development and upcoming particle emission limits in Europe have increased the need for detailed analyses of particle emissions of modern gasoline vehicles using gasoline direct injection (GDI) technology. Here the particle emission characteristics of modern GDI passenger cars were studied in a laboratory and on the road, with the focus on exhaust particle number emissions, size distributions, volatility and morphology.

EXPERIMENTAL

In total three modern gasoline passenger cars were tested (Table 1), of which vehicles 1 & 2 were studied in the laboratory and vehicle 3 the on-road (Karjalainen et al., 2014a; Karjalainen et al., 2014b; Rökkö et al., 2014).

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Year built</th>
<th>Technology</th>
<th>Tested in</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2011</td>
<td>GDI</td>
<td>Laboratory</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>2012</td>
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</tbody>
</table>

In the laboratory, the particle sampling was executed with a system consisting of a porous tube diluter, ageing chamber and an ejector diluter. Exhaust particles were measured in real-time with ultrafine condensation particle counters, an electrical low pressure impactor and an engine exhaust particle sizer (EEPS). The particle volatility was studied utilizing a thermodenuder at 265 °C. Exhaust particles were also collected and analysed with a transmission electron microscope.

In experiments on the road, similar instrumentation was used as in the laboratory. The test vehicle was chased with the “Sniffer” mobile laboratory.

CONCLUSIONS

Both during acceleration and steady conditions the number size distribution of non-volatile exhaust particles consisted of two modes, one with mean particle size below 30 nm and the other with mean particle size approximately 70 nm.

Results indicate that both of these particles modes consisted of soot but with different morphologies. Both in laboratory and on the road, significant emissions of exhaust particles were observed also during decelerations conducted by engine braking. In total particles during engine braking added up to 3–30% of total particle number emissions depending on the test routine. These particles are most likely originating from lubricant oil ash components. The semivolatile nucleation particles were observed in the laboratory experiments at high engine load conditions. Thus, in general, the studies indicate that modern gasoline vehicles can emit four distinctive types of exhaust particles. The differences in particle characteristics and formation should be taken into account in the development of emission control strategies and technologies and, on the other hand, in the assessment of the impact of particle emissions on environment and human health.

REFERENCES


Cytotoxicity caused by emission particles from different wood species


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Keywords: masonry heater, cytotoxicity, beech, birch, spruce

INTRODUCTION

Particulate air pollution affects public health negatively by causing cardiovascular and pulmonary disease and reducing life expectancy (Hoek et al., 2013). One of the most important sources of fine particulate air pollution is wood combustion and many studies point out that these emissions exacerbate asthma and other respiratory diseases (Naheher et al., 2007). Wood combustion emissions from different furnaces have been widely investigated. Both the appliances and user related practices in wood log combustion affect the emissions and their toxicity. However, the information on how different wood species affect these parameters is limited.

METHODS

Three different kinds of wood logs of beech, birch and spruce were combusted in batches in a modern soapstone masonry heater. Particulate emission samples were collected using a Dekati® Gravimetric Impactor (DGI) as described previously and the PM₁₀ fractions were pooled and extracted for chemical and toxicological analyses (Ruusunen et al., 2011).

Chemical analyses of the particulate samples were conducted and the particles’ ability to induce toxicological responses was tested using various assays of cytotoxicity (MTT, PI exclusion, Neutral Red Assay, Total Protein Content) in a human alveolar epithelial cell line (A549).

CONCLUSIONS

The emission particles from the combustion of different wood logs induced very distinct responses in A549 cells. Both the beech wood and the birch and spruce wood combustion samples induced a significant and dose-dependent reduction of the cell’s metabolic activity as measured by MTT-test (Figure 1). The PM₁₀ sample from the spruce combustion induced a reduction of the cells’ metabolic activity, but we did not find dose-dependency (Figure 1). Of the samples tested in this study, the PM₁₀ from beech wood combustion induced a significantly larger reduction of the cells’ metabolic activity than the PM₁₀ from birch or spruce combustion, even though the chemical composition of the samples differed only minimally. We found similar results in the other cytotoxicity assays.

Hence, we can conclude that when using a modern masonry heater for heating purposes, the wood log species affects the emissions significantly.

ACKNOWLEDGEMENTS

This work was supported by the Finnish Funding Agency for Technology and Innovation (Tekes), the European Regional Development Fund (ERDF), the University of Eastern Finland strategic funding, and the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE).

REFERENCES

Hygroscopic properties of nanoparticles produced from homogeneous nucleation of sulfuric acid and dimethylamine or α-pinene during CLOUD 7 campaign

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Keywords: Hygroscopicity, nano-HTDMA, nucleated nanoparticles, CLOUD

INTRODUCTION

Sulfuric acid, amines and oxidized organics play a significant role in the nucleation and initial growth of atmospheric particles. However, the properties of the freshly nucleated particles and the detailed pathways of their formation processes are still not clear. In this study, we determine hygroscopic properties of nanoparticles (10 and 15 nm) by using a nano-hygroscopicity tandem differential mobility analyzer (nano-HTDMA) at subsaturated conditions during the CLOUD 7 (Cosmics Leaving OUtdoor Droplet) experiments at CERN.

METHODS

Hygroscopic growth factor (HGF) is a measure of the diameter growth of particles at 90% RH compared with dry conditions ($d_{\text{dry}}$). Based on the HGF, the hygroscopicity parameter, $\kappa$, can be calculated using semi-empirical model introduced by Petters and Kreidenweis, 2007:

$$\kappa = \left[ \frac{\text{HGF} - 1}{\text{HGF}} \right] \left[ \frac{1}{5} \exp \left( \frac{A_{\text{HGF}} M_{w} T}{R \rho_{w} \sigma_{\text{sol}} HGF} \right) - 1 \right]$$

where $M_{w}$ is the molecular weight of water, $\sigma_{\text{sol}}$ is the surface tension of the solution, $R$ is the ideal gas constant, $T$ is the temperature, $\rho_{w}$ is the density of water.

CONCLUSIONS

The hygroscopicity decreased with increasing particle size as shown in Figure 1. In addition, a difference in $\kappa$ between sulfuric acid and sulfuric acid-dimethylamine increased. Our results suggest that the contribution of dimethylamine on particle growth increases with increasing size. This is likely due to the Kelvin effect.

![Figure 1. Comparison of $\kappa$ of 10 and 15 nm particles in the presence of sulfuric acid, sulfuric acid-dimethylamine, and sulfuric acid-organics produced by α-pinene oxidation (i.e. ozonolysis).](image)

ACKNOWLEDGEMENTS

We would like to thank CERN for supporting CLOUD with important technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. This research has received funding from the EC Seventh Framework Programme (Marie Curie Initial Training Network "CLOUD-ITN" no. 215072, MC-ITN "CLOUD-TRAIN" no. 316662, and ERC-Advanced "ATMNUCLE" grant no. 227463), the German Federal Ministry of Education and Research (project nos. 01LK0902A and 01LK1222A), the Swiss National Science Foundation (project nos. 200020_135307 and 206620_130527), the Academy of Finland (Center of Excellence project no. 1118615), the Academy of Finland (135054, 133872, 138951, 251427, 139656, 139995, 137749, 141217, 141451, 2720541, 259005, 264989), the European Research Council (Starting Grant 335478), the Finnish Funding Agency for Technology and Innovation, the Nessling Foundation, the Austrian Science Fund (FWF; project no. P19546 and L593), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/ 2010), the Swedish Research Council, Vetenskapsrådet (grant 2011-5120), the Presidium of the Russian Academy of Sciences and Russian Foundation for Basic Research (grants 08-02-91006-CERN and 12-02-91522-CERN), and the U.S. National Science Foundation (grants AGS1136479 and CHE1012293).

REFERENCES

Contribution of water to aerosol optical depth.

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Keywords: modelling, global, forcing, remote sensing

INTRODUCTION

Modelled direct radiative forcing of aerosol in global aerosol models varies between -0.06 to -0.49 W m⁻² making it currently one of the most uncertain factor in climate change (Shindell et al., 2013). The variance in aerosol direct radiative forcing is regionally even much larger indicating significantly different spatial difference in aerosol load. This can be seen in global maps of aerosol optical depth (AOD) in Figure 1. A significant fraction of aerosol optical depth comes from aerosol water which also varies significantly between different models. In this study, we investigate the reasons for these differences in the models. In this study, we investigate how differences in modeled aerosol composition, relative humidity, and size distribution contribute to differences in AOD and optical depth of aerosol water.

Figure 1. Aerosol optical depth modeled by a) ECHAM-HAMMOZ-SALSA model b) GOCART model.

METHODS

We compared Aerocom II model data for aerosol optical depth against those observed by Moderate-Resolution Imaging Spectroradiometer (MODIS) instrument on board of Terra and Aqua satellites. Modeled relative humidities were compared against observations from the Atmospheric Infrared Sounder (AIRS) flying on board NASA’s Aqua satellite.

CONCLUSIONS

According to preliminary results, modeled transport of aerosol has significant implications on zonal distribution of aerosol optical depth. Models that underestimate transport of aerosol towards poles also have lower AOD over high latitudes. The contribution of water to the AOD can be significantly higher in models with low poleward transport. However, it is not be sufficient to compensate low total aerosol optical depth.

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REFERENCES

Investigating the growth of atmospheric molecular clusters based on appearance times and collision-evaporation fluxes

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Keywords: molecular clusters, growth rate, new particle formation

INTRODUCTION

To estimate the climate effects of atmospheric new particle formation, it is essential to know how large fraction of freshly formed particles is able to grow to climatically relevant sizes (Kuang et al., 2009). For this reason, many methods have been utilized to deduce the growth rates of particles from measured particle size distributions (Y -Juuti et al., 2011). In this study, we use a dynamic cluster model to investigate how well one of these methods, based on appearance times of clusters, is able to describe the growth of a cluster population. We aim to answer to the following questions: 1) How well does the growth rate derived from the appearance times of clusters (AGR) correspond to the growth rate determined from the collision-evaporation fluxes between different cluster sizes (FGR)? 2) How important are the collisions of molecular clusters compared to monomer collisions for the growth of a cluster population?

METHODS

We simulated the time evolution of a cluster population up to 70 clusters (corresponding to 2 nm in mass diameter) in a one-component system using the Atmospheric Cluster Dynamics Code (ACDC). We determined FGR following the method by Olenius et al. (2014) and AGR with a method that has been used for experimental data (Lehtipalo et al., 2014). The model substance was assumed to have the properties of sulfuric acid, but the saturation vapor pressure was lowered to ensure that the collisions of small clusters significantly contribute to the growth. Thus, the model system mimics sulfuric acid driven particle formation assisted by a basic compound such as ammonia or amines. We grouped the clusters into size bins containing an equal number of clusters (in most simulations ten) for which we calculated the growth rates. The comparison of FGR and AGR in the conditions where clusters grow only by monomer additions and a resolution of a single molecule is assumed has been presented by Olenius et al. (2014).

A number of simulations was performed by varying the vapor monomer concentration, the magnitude of an external sink, the saturation vapor pressure, and the width of the size bins. In most of the simulations we assumed that the Gibbs free energy of the formation of clusters has a single maximum and no minima. However, in one simulation set a free energy surface containing a local minimum was used.

CONCLUSIONS

We observed significant differences between AGR and FGR. In the simulations where the free energy surface had no minimum, AGR was always higher than FGR. The AGR to FGR ratio was highest in the smallest size bin \((10^{-5} - 10^0)\), and lowest at the largest sizes \((-1.5 - 20)\). The ratio was lowest when the monomer concentration was high, the sink low and the saturation vapor pressure low, which all correspond to the conditions with high cluster concentrations. In these conditions, non-monomer collisions contributed significantly to the total fluxes between different size bins. The non-monomer fraction of the flux was highest in the smallest size bin \((2-30\%)\) and lowest at the largest sizes \((2-20\%)\).

When the free energy surface had a minimum, the ratio of AGR and FGR was slightly closer to one than in the simulations without the minimum. The ratio was highest in the second smallest size bin and lowest at the largest sizes. In these simulations, the non-monomer fractions of the fluxes were clearly higher than in other simulations. In the two smallest size bins the non-monomer fraction of the flux was ~99% and even at the largest sizes it exceeded 70%. Thus, in this case the growth of clusters seems to proceed mainly by the collisions of stable small clusters. Finally, we also found out that the width of the size bins affects the AGR to FGR ratio. When wider size bins were used, the ratio became higher due to higher values of AGR.

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REFERENCES


Portable ice nuclei counter SPIN: Key specifications, principle of operation and the first experiments

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Keywords: Ice nucleation, Ice nuclei counter, Diffusion chamber, SPIN.

INTRODUCTION

This abstract presents the key specifications of a recently developed portable ice nuclei (IN) counter instrument SPIN (SPectrometer Ice Nuclei), its principle of operation, first experiments and plans of ice nucleation experiments in the near future. The instrument, manufactured by Droplet Measurement Technologies (DMT), is the first commercially available IN counter and it uses continuous flow diffusion chamber (CFDC) technique. Currently five SPIN units have been manufactured so far, and our unit (number 5) will be used in experiments on both laboratory-produced and ambient aerosols.

THE INSTRUMENT

The SPIN is a portable IN counter where the icing conditions are created using the CFDC technique (Stetzer et al., 2008), where the aerosol flow is exposed to water vapour in temperatures below the freezing point. All parts of the instrument are fitted in one rack. Both walls of the IN chamber have independent refrigeration systems and thus the walls can be set to different temperatures. The temperature difference creates a diffusional vapour flux across the ice-coated chamber and saturation conditions can be regulated via adjusting the difference. Sample temperature can then be regulated via either cooling or heating the both walls simultaneously, while keeping this difference constant.

When the particles exit the IN chamber they are observed via using an optical 4-channel detector, where they are illuminated by linearly polarized laser beam of 500 mW in power and 670 nm in wavelength. The channels include size detection via scattered signal strength, two channels for parallel polarization (P1 for backscattering and P2 for forward scattering) and one for perpendicular (S1, backscattering). The polarization data is needed for separating the ice crystals from liquid water droplets, because the scattered light has a different polarization pattern depending on shape of the particle, i.e. spherical liquid droplets versus non-spherical ice crystals.

EXPERIMENT AND DEVELOPMENT PROGRAMME

The development of portable IN counters is relatively new and the published knowledge about the performance of these instruments is still limited (Chou et al., 2011). Therefore our experiment programme consists of starting the measurements using particles that have well-documented IN capabilities, such as ammonium sulphate and different mineral clay particles. Once validation experiments have been carried out the aim is to extend the research on various aerosol types, such as secondary organic aerosols (SOA) and real-life ambient aerosols in field campaigns.

In addition to currently ongoing testing and experimental studying we participate to development of the SPIN instruments and data analysis, in co-operation with DMT and other SPIN research groups. This co-operation includes e.g. intercomparison experiments between earlier SPIN units. The refrigeration system of all SPIN instruments will be upgraded shortly and our research includes studying possibilities of using the SPIN for measurements in an additional ice nucleation mechanism, immersion freezing.

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REFERENCES


Tracking of organic sources at Finnish boreal forest area

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Keywords: aerosol, chemical composition, organics, PMF

INTRODUCTION

Aerosol particles have adverse effects on health and climate (Haywood and Boucher, 2000; Naehler, 2007). Aerosol particles are originated from biogenic and anthropogenic sources. In remote boreal forest area, gaseous emissions related to both are connected to atmospherically important new particle formation (Kulmala, 2003).

The sources can be detected by tracking temporal variation of aerosols chemical composition in detail. The knowledge of sources can also be connected to other relevant atmospheric aerosol information like for instance formation mechanisms and aging.

METHODS

The measurements were conducted (61° 51’N, 24° 17’E) in Hyytiälä at SMEAR II (Station for Measuring Forest Ecosystem-Aerosol Relations) in Southern-Finland at early spring in 15.3-20.4.2011. HR-TOF-AMS (High Resolution Time-Of-Flight Aerosol Mass Spectrometer) was deployed to measure chemical composition of non-refractory aerosol particles with aerodynamic diameter of 40-1000 nm (Decarlo et al., 2006). Positive matrix factorization (PMF) was used to split the measured organics and nitrate ion fragments (NO\textsuperscript{+} and NO\textsubscript{2}\textsuperscript{+}) into groups according to their sources (Ulbrich, 2009). The origin of nitrate was tracked by calculating NO\textsuperscript{3}/NO\textsubscript{2}\textsuperscript{+} ratio. Supporting measurement data from trace gas constituents, particle size distributions and meteorological parameters were used for the interpretation of AMS data.

CONCLUSIONS

Average mass loading during the campaign was 1.8 \( \mu g/m^2 \) from which organics 49 \%, sulfate 22 \%, ammonium 10 \%, nitrate 7 \%, black carbon 11 \% and chloride < 1 \%. Organics and nitrate were split by PMF into sources of SV-OOA (Semi Volatile – Oxidized Organic Aerosol; local source), highly aged LV-OOA (Low Volatile – OOA; highly aged), NO- and sawmill-factor (see Fig. 1). Sawmill-factors NO\textsuperscript{3}/NO\textsubscript{2}\textsuperscript{+} ratio of 16.9 corresponds to organic nitrates and NO-factors 2.4 to ammonium nitrate. Sulfate was mainly consisting of ammonium sulfate that was related to long-range transported aerosol.

Diurnally ammonium nitrate and SV-OOA increased during the night-time by settling down boundary layer and LV-OOA increased by day-time when photo-oxidation increased and particles grew in an organic solvent. Newly found particulate organic nitrates formed from the local sawmill emissions. The results were in line with previously published results at the site.

REFERENCE

Particulate and gaseous emissions of birch, beech and spruce combusted in a modern masonry heater

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Keywords: modern masonry heater, wood combustion emissions, PM1, organic emissions

INTRODUCTION

Batch combustion devices are known to produce high amounts of particulate and gaseous emissions. This kind of appliances are commonly used as a supplemental heat sources in Nordic countries as well as in other cold European countries. The EU’s forthcoming objective to increase the share of renewable energy in total energy consumption is likely to further increase the small scale biomass combustion.

The emissions from batch combustion devices are known to entail relatively large proportions of black carbon and organic aerosols. A part of this primary organic aerosol is known to form secondary organic aerosol in the atmosphere.

METHODS

We compared the emissions from three different European wood species combusted in a modern masonry heater. In each experiment six batches (2.5 kg each) of wood logs were combusted during four hours. In total 17 experiments were conducted (7 with birch, 6 with beech and 4 with spruce).

From undiluted flue gas the concentrations of O2, CO2, CO, NOx, OGC were measured with gas analyser system (ABB) and fourier transform infrared spectroscope (FTIR, Gasmet). Particle number emissions, mass emissions and number-size distributions were measured from diluted flue gas with electrical low pressure impactor (ELPI, Dekati), scanning mobility particle sizer (SMPS, TSI) and fast mobility particle sizer (FMPS, TSI). The chemical composition of fine particles was also characterized with an aerosol mass spectrometer (Sp-HR-ToF-AMS, Aerodyne). In addition, PM1 samples were collected on Teflon and quartz filters for gravimetric and elemental analysis. From filter samples also the concentrations of organic and elemental carbon (OC, EC) were conducted.

Generally, the combustion conditions had only minor variation for a single wood species in consecutive experiments, showing a good repeatability.

The emissions were observed to vary significantly between the batches and even within a batch, which is considered typical for this kind of combustion process. The highest total PM as well as organic emissions were measured during the first batch. In addition, the ignition of the batches generated typically large amounts of gaseous and particulate organics. The PM composition was dominated by elemental carbon (soot). However, during char burning the PM was mainly composed of alkali metal salts.

Table 1. Average total emissions of refractory black carbon (rBC), elemental carbon (EC), organic aerosol (OA) and fine particulate matter (PM1) normalized to 13% O2.

<table>
<thead>
<tr>
<th></th>
<th>rBC</th>
<th>EC</th>
<th>OA</th>
<th>PM1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birch</td>
<td>40</td>
<td>54</td>
<td>24</td>
<td>68.4</td>
</tr>
<tr>
<td>Beech</td>
<td>13</td>
<td>30</td>
<td>12</td>
<td>39.7</td>
</tr>
<tr>
<td>Spruce</td>
<td>11</td>
<td>13</td>
<td>8</td>
<td>21.9</td>
</tr>
</tbody>
</table>

The results indicate that in the development of cleaner batch combustion units, more attention should be paid on ignition periods of the wood batches. The modern masonry heaters tend to generate PM with relatively low OC/EC ratios.

ACKNOWLEDGEMENTS

The authors acknowledge the strategic funding of the University of Eastern Finland for project sustainable bioenergy, climate change, Academy of Finland and Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE).
Particle chemistry of ship emissions in Gothenburg, Sweden

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Keywords: fuel sulphur, AMS, ship lane

INTRODUCTION

Sulfur legislation in Sulfur Emission Control Areas (SECA) is helping to reduce emissions of sulphate containing particles from ship traffic. Before 2010, 1.5 weight % sulphur fuel content was allowed in the Baltic Sea, and between 2010 and December 2014, 1 % sulphur content was allowed. Beginning in 2015, the sulphur content limit will be further reduced to 0.1%. Hence, there is an opportunity to investigate the consequences in terms of particle emissions after each reduction step.

METHODS

A measurement campaign was undertaken from October to November 2014 at the inlet to the Gothenburg harbor in Sweden (Figure 1). The site is 1 to 2 minutes downwind of passing ship plume emissions during occasions with southerly winds.

Several chemical compounds have been measured along with particle number size distribution. A Soot Particle Aerosol Mass Spectrometer (SP-AMS) was used to measure organics, sulfate, soot, nitrate, ammonia, and chlorine concentrations. Light absorption was measured with a Photo-Acoustic Soot Spectrometer at three wavelengths (PASS-3), and with a Multi-Angle Absorption Photometer MAAP 5012 at 637 nm.

CONCLUSIONS

The results show that the sulphate emissions have significantly decreased compared to measurements in 2006, where both low-sulfur fuel and high-sulfur fuel ships have been characterized (Figure 2).

A potential aerosol mass (PAM) chamber and a cloud condensation nuclei counter (CCNC) has also been used to study the ageing and the cloud forming properties of particles in the campaign.

A similar measurement campaign is planned for 2015 to investigate the change in emissions resulting from the new sulphur regulations. Additional measurements of aged ship emissions are also planned during 2016 in southernmost Sweden.

ACKNOWLEDGEMENTS

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REFERENCES

Reducing approximation errors in cloud droplet formation in a global climate model

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Keywords: aerosol, modelling, random forest, echam

INTRODUCTION

Because of the high computational cost involved in including aerosols into global climate models, aerosol microphysical processes are usually highly parametrized and aerosol size distributions are represented in a relatively coarse manner. These kind of model simplifications introduce so-called approximation errors which may significantly affect the impact that aerosols have in climate models. Here we apply the Random Forest regression algorithm to correct the approximation errors that occur in cloud droplet formation in the global climate model ECHAM-HAMMOZ.

METHODS

For our simulations we use the general atmospheric circulation model ECHAM-HAMMOZ (ECHAM6.3-HAM2.2) at a horizontal resolution of T63 (roughly 1.9° by 1.9°) and a vertical resolution of 31 hybrid sigma-pressure levels (Roeckner et al. (2003); Roeckner et al. (2006)).

Aerosol processes are modeled within the HAM-SALSA module which describes the aerosol size distribution using 7 sectional size bins (Bergman et al. (2012)). The model describes all known aerosol processes relevant to atmospheric science, namely emissions, removal, aerosol microphysics, chemistry, radiative effects, and aerosol-cloud interactions. The aerosol compounds included in the model are sulfate, organic carbon, sea salt, black carbon, and mineral dust. CCN activation is described explicitly in the model using the Abdul-Razzak-Ghan parametrization (Abdul-Razzak et al. (1998)).

The Random Forrest (RF) algorithm (Breiman (2001)) uses training data from an exact model to construct a set of regression trees, which can then be used to correct the approximation errors of the simplified model. The computed correction term depends on a set of specified input parameters and on the output of the simplified model. Here we use the RF approach to correct the number of activated cloud condensation nuclei (CCN) in ECHAM-HAM. The RF regression trees have been generated using the aerosol module SALSA in a chamber setup using a much finer resolved aerosol size distribution (70 size bins) (Lipponen et al. (2013)).

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A new method for determining collision and evaporation rates from measured cluster distributions

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Keywords: Markov chain Monte Carlo, molecular clusters, data analysis, mass spectrometry

INTRODUCTION

Both experimental and theoretical tools for studying the first steps of particle formation have been developing rapidly in the past few years. High-resolution mass spectrometers have enabled the detection and characterization of small electrically charged molecular clusters (Junninen et al., 2010), and on the other hand, kinetic simulations using quantum chemistry–based evaporation rates have produced cluster distributions (Olenius et al., 2013) and formation rates (Almeida et al., 2013) that are in qualitative agreement with experiments. However, measurements and simulations have mostly remained two separate approaches for understanding cluster formation instead of truly complementing each other.

The present study introduces a new approach for analyzing experimental cluster distribution measurements using state-of-the-art kinetic modeling. The method is applied here to negatively charged sulfuric acid–ammonia clusters, but it can be used for any set of clusters as no prior knowledge about the compounds is needed.

METHODS

The basis of the method is to compare the experimental cluster distribution to simulation results in order to find rate constants that best reproduce the observations. As there are tens of unknown rate constants even for a relatively small set of clusters, and as the cluster concentrations depend on them in a highly nonlinear way, the task of finding optimal values for the parameters is tackled by Markov chain Monte Carlo (MCMC).

The time evolution of the cluster concentrations is simulated by ACDC, a code that solves the birth-death equations taking into account all possible collision and evaporation processes as well as ion production and external losses. The rate constants are not taken from any theory as in our previous modeling studies (Olenius et al., 2013; Almeida et al., 2013) but are instead treated as free parameters that are varied by MCMC.

CONCLUSIONS

The method was first tested by analyzing simulated cluster distributions. In this case the “correct” values of the collision and evaporation rates are known, and it can be examined whether the analysis of the cluster distributions gives these correct values. It was found that a large fraction of the rate constants could be determined from the analysis. More specifically, the method performed well for rate constants corresponding to rate-limiting steps on the formation pathway, while many of the less important rate constants could not be determined. In addition to the collision and evaporation rates, also the ion production rate and wall loss rate as well as fragmentation probabilities in the inlet of the mass spectrometer were treated as unknown parameters and their values could be successfully extracted from the analysis.

The new analysis method was also applied to the experimental cluster distributions measured at CLOUD (Olenius et al., 2013). The ammonia concentration was below the detection limit and thus unknown in many of the experiments, leading to uncertainties in analyzing the cluster distributions. Some tentative results will, however, be presented.

The new method shows great potential as a powerful tool for analyzing cluster distribution measurements.

ACKNOWLEDGEMENTS

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REFERENCES


Feedback mechanisms modifying the aerosol concentrations in the changing polar climate – new biogenic and anthropogenic sources for secondary aerosols

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Keywords: Polar regions, new particle formation, climate change, CCN

Both northern and southern polar regions are very sensitive to the ongoing climate change. The changes in the interactions between the atmosphere, biosphere and cryosphere in these regions have inevitable consequences to global climate as well. Aerosol-cloud-climate interactions pose the largest uncertainties related to estimating our future climate. In order to be able to quantify these, we first need to know how the sources of aerosols will change in the future.

There are several feedback mechanisms related to warming Arctic that have the potential to alter the cloud droplet number concentrations (CDNC) (Fig. 1). Here we introduce four such mechanisms, related to (i) the increase of meltwater, (ii) increase of human activity and (iii) decrease of the Arctic sea ice.

First feedback loop is related to the increase of meltwater in glaciated and snow covered areas during the summertime as the climate warms. This increases the emissions of biogenic volatile organic compounds (BVOC) which in turn may both increase the formation and growth of secondary organic aerosols and finally, cloud condensation nuclei (CCN). This has been shown to contribute significantly to the production of CCN in glaciated areas (Kyrö et al., 2013). This feedback loop also includes the increased terrestrial BVOC emissions due to increasing temperature (Paasonen et al., 2013).

On the other hand, decreasing Arctic sea ice supposedly attracts more marine activity as it opens up new, faster shipping routes and allows oil and gas drilling from new areas. The increased human activity brings more anthropogenic SO₂ emissions to the Arctic. The concentrations of CCN and CDNC can either increase or decrease depending on the balance between SO₂ increasing the formation rate but at the same time, decreasing the growth rate (GR) by increasing condensation sink (CS). Long-term study of sulphur pollution originating from Kola Peninsula shows that at least in Eastern Lapland, higher SO₂ leads to more days of active new particle formation (NPF) and increases the concentration of potential CCN (Kyrö et al., 2014).

Decreasing Arctic sea ice increases the fluxes of heat and moisture into the atmosphere. As a consequence, the atmospheric transport and snowfall rates in Siberia and Europe may change. Since snow is an efficient scavenger (Kyrö et al., 2009), this has a potential to decrease the CCN and CDNC concentrations in those areas and decrease the pollution transport into the High Arctic from lower latitudes. On the other hand, condensational growth is important in the west to east transport over Boreal forests (Vä å nä et al., 2013). This, combined with increased atmospheric transport times due to slowing of the Polar jet can allow the particles to grow larger and more or them to reach CCN sizes.

![Diagram](Image)

**Figure 1.** Feedback mechanisms related to warming Arctic.

**ACKNOWLEDGEMENTS**

This work has been supported by the Finnish Center of Excellence (The Centre of Excellence in Atmospheric Science – From Molecular and Biological processes to the Global Climate) and the Nordic Center of Excellence CRAICCC (Cryosphere-atmosphere interactions in a changing Arctic climate)

**REFERENCES**

Effects of the large volcanic eruption during the solar radiation management

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Keywords: Geoengineering, Climate Modelling, Volcanic eruption, Sulfate aerosols.

INTRODUCTION
Solar radiation management (SRM) by stratospheric sulfur injection is one of the most discussed and probably the most cost effective geoengineering method. Injecting sulfur to the stratosphere could be seen as an analogy of large volcanic eruptions, where large amounts of sulfur dioxide are released into the stratosphere. In the atmosphere SO₂ oxidizes and forms aqueous sulfuric acid aerosols which reflect incoming solar radiation back to space.

If SRM is ever used to cool the climate it is possible that a huge volcanic eruption could happen also during the SRM. This would lead temporally to a very strong cooling effect when the sulfate from both geoengineering and the volcanic eruption could reflect solar radiation. However if the volcanic eruption takes place during the SRM, the atmospheric conditions are different compared to current conditions because of sulfate from sulfur injections. Thus effects from the volcanic eruption during the SRM cannot be estimated only by studying the volcanic eruption in normal circumstances. Here we study the effects of the volcanic eruption during SRM by using two climate models.

METHODS
Simulations have been performed in two steps. In the first step, we have used the aerosol-climate model MAECHAM5-HAM-SALSA to define aerosol fields. The model is the global atmospheric model which describes aerosol size distribution by 10 size bins and calculates all major aerosol physical processes. In the second step of the study we have performed climate simulations using Max-Planck-Institute’s Earth system model (MPI-ESM) [Giorgetta et al., 2013] by using aerosol fields defined by MAECHAM5-HAM-SALSA. We have studied scenarios of volcanic eruptions in two different locations and seasons and during the SRM sulfur injections and without injections.

CONCLUSIONS
Sulfate burden and radiative forcing after the volcanic eruption decrease clearly faster if volcanic eruption happens during the geoengineering injections. If a volcano erupts concurrently with a geoengineering sulfur injections, sulfur from the eruption does not only form new particles but it also condenses into pre-existing particles. This leads to larger particles which lifetime is shorter. In addition because there is less and larger particles, the effect to the short-wave radiation is smaller. As radiative cooling effect is smaller after volcanic eruption during SRM than normal atmospheric conditions, the global mean temperature would have returned to the level before the eruption faster which can be seen from figure 1.

The season when the eruption occurs has only a small contribution to the global radiative effect if volcano is erupted in the Tropics. In the Arctic area the eruption in January would lead clearly largel global mean radiative forcing than eruption in July.

Figure 1. Temperature change compared to level before volcanic eruption in normal atmospheric conditions (black line) and during SRM (red line). Solid lines are mean values of the four separate simulations (dashed lines)

ACKNOWLEDGEMENTS
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REFERENCES
Formation of ultrafine AuNPs in the aerosol synthesis

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Keywords: gold nanoparticles, spray synthesis

INTRODUCTION

Gold nanoparticles (AuNPs) and arrays are promising candidates for applications in various fields including electronics, optoelectronics, catalysis and biology (Zhou et al. 2009). AuNPs are stable in air and light. However, gold forms bonds easily with itself, leading to formation of large clusters and agglomerates.

There are a number of methods used for the preparation of AuNPs, including sol-gel, layer-by-layer self-assembly, and aerosol assisted methods (Daniel and Astruct 2004). Aerosol assisted processes (e.g. spray pyrolysis) are well-known methods for the production of submicron particles. However, the particles produced with the aerosol processes are often irregular agglomerates (Magnusson et al. 1999). In this paper we present an atmospheric pressure aerosol synthesis method for the preparation of stable ultrafine gold particles.

METHODS

Homoleptic alkynyl gold complex (AuC₂R)₁₀, (R=2,6-dimethyl-4-heptanol) was used as a precursor for the aerosol synthesis of the particles (Koshevoy et al. 2012). The Au precursor was dissolved in ethanol or hexane and atomised with a constant output atomizer (model 3076, TSI Inc.) (Lähde et al. 2014). Nitrogen carrier gas was used to carry the atomized droplets into the heated zone of the reactor. The temperature of the reactor was varied between 200 ºC and 800 ºC. A systematic investigation of the influence of the process parameters on the powder characteristics, including the particle and crystallite sizes, and the surface properties, was carried out.

RESULTS AND CONCLUSIONS

Figure 1 a-c shows TEM images of the AuNPs prepared from the ethanol and hexane precursor solutions at different temperatures. FTIR gas phase analysis revealed that AuNPs produced from the ethanol solution were formed by ethanol oxidation (Lähde et al. 2014):

\[ \text{C}_2\text{H}_6\text{OH} + (\text{AuC}_2\text{R})_{10} \rightleftharpoons \text{CH}_3\text{CHO} + \text{AuNP} + \text{e.g. HC}_2\text{R} \]

The ethanol reduction of the Au precursor by was excluded in the hexane solution (Lähde et al. 2014). However, the properties of the produced particles were very similar than the particles obtained with the ethanol solution (Figure 1 d-f). This was due to the intramolecular reactions of (AuC₂R)₁₀ complex. The precursor has hydroxylaliphatic alkynyl ligands, C₂–(OH)C₉H₁₈. Thus, the precursor itself possesses the HO– groups, which may induce the reduction of the gold and the simultaneous oxidation of the ligand to give a carbonyl containing –C(=O)– organic side chains.

Figure 1. AuNPs produced from ethanol (a-c) and hexane (d-f) precursor solutions at temperatures between 200 and 800 ºC.

The size of the primary AuNPs varied between 2.4 and 4.1 nm. In addition, the particles produced above 400 ºC were phase-pure gold, with an outer layer of carbon forming above 600 ºC. At 800 ºC, thermal decomposition of the carbon compounds including the solvents was detected with the FTIR gas phase analyser.

ACKNOWLEDGEMENTS

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REFERENCES

Simple diluting sampling method for type testing of particulate mass emissions from small-scale wood combustion appliances

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Keywords: combustion emissions, sampling, dilution

INTRODUCTION

Most of the present methods in testing of small wood combustion installations for particle emission measurements are based on sampling of particles directly from hot flue gas on a heated filter without dilution. These methods do not fully take into account the semivolatile organic fraction of particulate matter and includes also coarse particle fraction, over 10 µm, which are not inhalable. Moreover, many chemical analyses suffer from this collection method making it difficult to include any additional analyses in the future.

Diluting the combustion flue gas before sampling has several advantages; it stabilises the sampling conditions, enables easier use of impactors and other aerosol instruments, as well as various chemical analysis methods, and it takes better into account the particulate organic fraction. Thus, diluting methods are widely used in scientific studies and also vehicle testing applies dilution methods in type testing.

METHODS

A simplified sampling system applying dilution was designed and tested in several combustion experiments at University of Eastern Finland. The system includes a heated probe placed in the chimney, porous tube diluter, PM$_{2.5}$ impactor and a stainless steel filter holder (Fig. 1). 90 mm PTFE filters were used in the tests to ensure sufficient capability of PM collection in various combustion conditions. Flow rates are automatically adjusted using mass flow controllers. Dilution ratio is measured based on CO$_2$ concentrations in the flue gas and in the diluted sample. A masonry heater and a pellet boiler were used as combustion emission sources in the experiments.

CONCLUSIONS

The simplified diluting PM sampling system for small combustion installations was found to work properly when both batch combustion emissions and pellet boiler emissions were tested. Comparing the system with a scientifically validated system of porous tube diluter and ejector diluter revealed that the results are well comparable.

In addition, the experiments revealed that accurate mass flow controllers are needed both for the dilution air and for the control of total flow, to ensure proper measurement accuracy and repeatability. It was additionally evident that dilution ratio needs to be determined by CO$_2$ concentrations, instead of using only flow control in the system. Heated tube before dilution was found to stabilize sample temperatures and thus the dilution behaviour in the highly variable batch combustion process.

A simple PM sampling system is needed to improve the scientific validity of the PM experiments in type testing of small combustion installations. With this method, it is possible to include for example an analysis of polycyclic aromatic hydrocarbons or other particulate organic compounds into the testing standard in the future.

ACKNOWLEDGEMENTS

This work is part of the “Common European method for the determination of particulate matter emissions of solid fuel burning appliances and boilers (EN-PME-TEST)” project. This work is supported by TEKES – the Finnish Funding Agency for Innovation.
Aging of exhausts from diesel vehicle and pellet boiler, and their mixture in an environmental chamber

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Keywords: diesel, pellet boiler, exhaust, aging, environmental chamber

INTRODUCTION

Aerosols are known to induce health and climate effects, which depend on their physicochemical properties. In the atmosphere the aerosol properties change in transformation processes, which can be studied in environmental chambers.

METHODS

Diluted exhausts of a diesel vehicle, a pellet boiler burning softwood pellets, and their mixture was injected into a 29 m³ environmental chamber. In some experiments also ozone, nitrous acid, acting as a hydroxyl radical (OH) precursor, and/or alphapinene was injected. The mixture was aged for 4 hours under UV irradiation. During the aging the size, number concentration, hygroscopic growth factor (HGF), chemical composition, morphology, optical properties, and mixing state of the particles, as well as concentration of nitrogen oxides, sulfur dioxide, ozone, selected ions, and volatile organic compounds in the gas phase were monitored.

CONCLUSIONS

The mobility and projected area equivalent diameters of the particles from both sources, both separately and in the mixture, increased from 80–90 to 120–130 nm during aging. Meanwhile, the number concentration decreased, but aerosol volume increased by 10–30 %.

The initial mass concentration was 45 (pellet) or 35 µg/m³ (diesel). The concentration of particulate organics increased from 4 to 12 µg/m³ (pellet) or remained at 2 µg/m³ (diesel). The increase in organics originates from secondary organic aerosol (SOA) formation, which is known to be more intense at low nitrogen monoxide (NO) concentrations. The initial NO concentrations were 16–46 (pellet) and 81–143 ppb (diesel).

The concentration of particulate nitrate increased from 1 to 8 µg/m³ (pellet) or was very low (diesel). The increase was faster when OH was present (Figure 1). The HGF for 100 nm particles was initially and remained at 1.55–1.60 (pellet), indicating very hygroscopic particles, or remained at 1.01–1.03 (diesel), indicating hydrophobic particles. A small decrease in the fractal dimension of pellet burner exhaust particles was seen.

The evolution of the mixed aerosol was a combination of the separate emissions. Both more and less hygroscopic fractions were seen, and the particles from each source could be separated from the electron micrographs. The HGF of the less hygroscopic fraction increased to 1.05, while that of the more hygroscopic fraction decreased from 1.60 to 1.45 or as low as 1.35 when alphapinene was present. The increase in particulate organics was less than (the expected) 50 % of that in pellet boiler exhaust, indicating that the high NO concentration of the diesel exhaust inhibits SOA formation.

In conclusion, the diesel vehicle exhaust is quite passive during aging while the pellet boiler exhaust produces SOA and particulate nitrate. In the mixture the particles are externally mixed, whereas the gas phases mixed and affected, e.g., the SOA formation potential of the individual emissions.

ACKNOWLEDGEMENTS

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Effective density and morphology of particles emitted from wood combustion

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Keywords: effective density, particle characterization, wood combustion

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Effective density ($\rho_{\text{eff}}$) of airborne fine particles is one feature in describing their behaviour in the ambient air and in human respiratory track. In this study (Leskinen et al. 2014) effective density ($\rho_{\text{eff}}$) was defined as follows

$$\rho_{\text{eff}} = \frac{m_p}{\sum n_i d_{\text{in}}^{3} \rho_{\text{in}}}$$

where $m_p$ = mass of individual particle, $d_{\text{in}}$ = mobility equivalent diameter.

Often, in aerosol science, particles are assumed to have a unit density due to simplification or lack of knowledge. However, the assumption can be misleading. For example, Wierzbicka et al. (2014) showed that the lung deposition dose of particle mass can be overestimated by 132 % if unit density is used instead of size dependent density.

In addition, the particle density is the link between electrical mobility and aerodynamic diameter. The results from impactors and classifiers can be compared if the density function is known.

Moreover, single particle mass or effective density values can be used to calculate mass-mobility exponent, which is to some extent related to fractal dimension (Sorensen 2011).

$$\rho_{\text{eff}} = K' d_{\text{in}}^{D_{\text{fm}}}$$

where $D_{\text{fm}}$ is mass-mobility exponent and $K'$ is equation constant.

In this study, we measured the effective density functions and mass-mobility-exponents of wood combustion emitted fine particles. The batch combustion appliance was a modern masonry heater which was operated with beech, birch and spruce wood logs. The studied cases were ignition (I), ignition of second batch (O), main combustion (C) and glowing embers phase (E). Continuous combustion appliance was modern pellet boiler. Two different softwood pellets were used (A and B).

The densities were measured using an Aerosol Particle Mass Analyzer (APM, Kanomax) and a Scanning Mobility Particle Sizer (SMPS, TSI) in series. Furthermore, a custom-made sampling chamber (volume 60 l, Ihalainen et al., 2012) was applied to overcome the effects of variations of combustion process. The chamber was filled with sample aerosol and then disconnected from the filling line. Measurements were done with the sample contained inside the chamber. Filtered air was used to replace the sample taken from the chamber.

Figure 1: Effective density of particles emitted from wood combustion.

The combustion conditions were found to affect the effective density and morphology of particles. In addition, there was a negative correlation between effective density and particle size in cases I, C and pellet A. In conditions O, E and pellet B a negative size correlation was not observed.

As a conclusion, no single value (unit or any other) can be used for effective density of wood combustion particles. Rather, effective density function should be determined for each combustion cases or conditions separately.

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Exposure to microbial compounds from waterpipe tobacco smoke

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Keywords: bioaerosol, exposure, lung deposition, effective density

INTRODUCTION

Cigarette tobacco contains large amounts of bacteria as well as molds and the smoke is rich in microbial compounds (Larsson et al., 2008). However, there have been no studies on the possible presence of microbe-derived substances in waterpipe tobacco and smoke. Because of the significantly lower temperature of the tobacco in a waterpipe compared to a cigarette, microbial substances may be more efficiently preserved in the smoke. The aim of the present study was to measure some selected microbial compounds in waterpipe smoke and to estimate the respiratory tract deposition.

METHODS

Second hand waterpipe and cigarette smoke was studied from 60-120 minute smoking sessions in a 22 m³ stainless steel chamber. In addition, mainstream and sidestream waterpipe smoke was machine-generated. Waterpipe smoke was analysed for bacterial lipopolysaccharide (LPS) and fungal ergosterol. The aerosol in the chamber was also characterized for particle size distribution in the range 10-650 nm with a scanning mobility particle sizer (SMPS) and mass concentration with a tapered element oscillating microbalance mass concentration (TEOM, Ruprecht & Patashnik Inc.). The effective density of the particles in the size range 70-420 was measured with an aerosol particle mass analyzer (APM, model 3600, Kanomax, Japan). The respiratory tract deposition of the second hand smoke particles was estimated based on the Multiple Path Particle Dosimetry (MPPD) model (version 2.11; Chemical Industry Institute of Toxicology, Research Triangle Park, NC).

CONCLUSIONS

This is the first time that waterpipe smoking has been shown to create a bioaerosols (Table 1).

Table 1. Amounts (mean) of total particulate matter (TPM), ergosterol, and LPS in smoke per machine waterpipe smoking session (n = 10).

<table>
<thead>
<tr>
<th></th>
<th>Mainstream</th>
<th>Sidestream</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPM (mg)</td>
<td>1870 (310)</td>
<td>Not available</td>
</tr>
<tr>
<td>Ergosterol (ng)</td>
<td>84.4 (51.2)</td>
<td>0.64 (0.82)</td>
</tr>
<tr>
<td>LPS (pmol)</td>
<td>1800 (300)</td>
<td>17.0 (4.7)</td>
</tr>
</tbody>
</table>

These results are significant since there is a known association between bioaerosols and respiratory disorders such as chronic obstructive pulmonary disease (COPD). The effective density of the second hand smoke particles is shown in Figure 1. The limited decrease of effective density with size is consistent with incomplete combustion, but may also be due to particle restructuring during inhalation. Almost 50% of the particles deposit in the pulmonary region of the lungs.

A comprehensive description of the study is provided by Markowicz et al. (2014).

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Estimation of partitioning activity coefficients for organic acids

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Keywords: Secondary Organic Aerosols (SOA), activity coefficient, Mass spectrometry

INTRODUCTION

Organic aerosols are one of the major constituents in ambient aerosols and can be found in aerosols all over the globe (Jimenez et al., 2009). Organic chemistry in the atmosphere is complex (Hallquist et al., 2009), e.g. it is difficult to describe the dynamics on how compounds partition between the gas and the particle phase. This might be one reason why theoretical estimates of organic aerosol concentrations are generally lower compared to what is measured in the field (Volkamer et al., 2006).

One of the reasons for the underestimation in models can be due to the very often made assumption that the activity coefficient, $\gamma_i$, is unity. To improve the knowledge on this issue we have investigated experimentally how organic acids partition between the gas and the particle phase.

METHODS

The measurements were made in Hyytiälä with a FIGAERO (Filter Inlet for Gas and AEROsol) coupled to a HRTof-CIMS (High-Resolution Time of Flight Chemical Ionization Mass Spectrometer) (Lopez-Hilfiker et al., 2013). To detect the organic acids acetate ions were used as reagent ion for the Chemical Ionization (Veres et al., 2008).

Partitioning, i.e. how compounds are distributed between the gas and the particle phase, has been described by Pankow (1994):

$$K_i = \frac{[i]_{\text{particle}}}{[i]_{\text{gas}} \cdot M_{\text{org}}} = \frac{RT}{MW_{\text{om}} \cdot \gamma_i \cdot p_i^0}$$

$K_i$ is the partitioning coefficient, $M_{\text{org}}$ the aerosol organic mass concentration, $[i]_{\text{particle}}$ and $[i]_{\text{gas}}$ are the concentration of compound $i$ in particle and the gas phase respectively, $p_i^0$ is the saturation vapor pressure, $\gamma_i$ the activity coefficient, $MW_{\text{om}}$ the mean molecular mass of the particle constituents, $R$ the gas constant and $T$ the temperature.

The concentration in the gas and the particle phase ($[i]_{\text{particle}}$ and $[i]_{\text{gas}}$) can be measured with the FIGAERO-HRTof-CIMS and $M_{\text{org}}$ can be measured with an Aerosol Mass Spectrometer. The average weight of the products in the particle phase, $MW_{\text{om}}$, is estimated to be 180g/mol. If the temperature is monitored the product of $\gamma_i$ and $p_i^0$ can be estimated. Furthermore, if the saturation vapor pressure, $p_i^0$, is known an estimation of the activity coefficient, $\gamma_i$, is possible, Figure 1.

CONCLUSIONS

A wide range of organic acids from monoterpene oxidation have been identified. Utilising data on the saturation vapour pressures the activity coefficients have now been estimated, and will be presented together with their implications for model/measurement discrepancies

ACKNOWLEDGEMENTS

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Filterbased TD-GC-MS Analysis of Organic Aerosol

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Keywords: aerosol, filter, analysis, composition

INTRODUCTION

Atmospheric aerosols have an important impact on climate and human health, which drives a significant amount of research into their composition. However, determining the composition of these particles is faced with many challenges because of the physical and chemical processes that these aerosols undergo. A wide variety of mass spectrometric techniques are being utilized, amongst these gas chromatography mass spectrometry (GC-MS)(Prather et al., 2010, Lashkin et al., 2012).

Feilberg et al. (2014) developed a method where an aerosol sample was collected on a filter, rolled up and inserted into an inert coated steel tube prior to thermal desorption. This allowed for detection of the organic matter in particles using a TD-GC-MS. However it is important to note that boiling point, GC column and thermal stability determines which compounds can be detected.

Our proposed method aims at improving the ease of sampling while reducing possible artefacts from sample handling thereby also allowing non-scientific personnel to handle sampling. This could be important for quantifying industrial pollutants and their aerosol emissions.

METHODS

Four identically sized, circular sections of quartz filters were inserted into a stainless steel tube as seen in Fig. 1. Collection efficiency of these quartz tubes was tested by atomizing phthalic acid using a TSI Atomizer, size selecting different particle sizes with a SMPS and passing them through a tube before detecting the number of particles penetrating the filters with a CPC.

![Figure 1. Stainless steel tube with four quartz filters held in place by stainless steel grids.](image)

In theory, both the Tenax TA and quartz filter tube should collect aerosols, thus a parallel setup is used to account for false positives on the quartz filter tubes from gas phase species, see Fig 2. Organic aerosol was generated using α-pinene ozonolysis in a flow-tube like setup. The composition of these particles was measured using TD-GC-MS.

![Figure 2. Two-by-two parallel setup for sample collection with one leg containing two Tenax TA tubes in series and a quartz filter tube followed by a Tenax TA in the other leg.](image)

CONCLUSIONS

As seen in Table 1, the tubesampler is able to collect particles very efficiently. From the remaining data analysis, it needs to be determined which organic aerosol constituents can be detected using this new method.

<table>
<thead>
<tr>
<th>Diameter nm</th>
<th>Mean (#/cm³)</th>
<th>STD (#/cm³)</th>
<th>Col. Eff. %</th>
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</thead>
<tbody>
<tr>
<td>20</td>
<td>3.5</td>
<td>1.0</td>
<td>98.4</td>
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<tr>
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REFERENCES

Using the Monte Carlo Markov Chain method to estimate contact parameter temperature dependence

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Keywords: Heterogeneous nucleation, deposition mode nucleation, Monte Carlo Markov Chain

INTRODUCTION

Wide temperature range datasets on deposition mode ice nucleation have revealed a strong dependence of the contact parameter \( m \) on temperature. This dependence varies from linear to exponential, depending on the experiment and the temperature range. We have analyzed three datasets using a Monte Carlo Markov Chain (MCMC) method. The used method allows us to test and evaluate different functional forms for the temperature dependence of the contact parameter. This study (Määttänen and Douspis, 2014) provides a new framework, valid even for very small ice nucleus sizes, for analyzing heterogeneous nucleation datasets.

METHODS

We perform a data inversion by finding the best fit to the measured data simultaneously at all points for different functional forms of the temperature dependence of the contact angle (“\( m \)-models”). The method uses a full nucleation model (Määttänen et al., 2005; Vehkamäki et al., 2007) to calculate the observables at each data point. For the moment, only single-\( m \) deposition mode nucleation is included.

We have focused on certain (Iraci et al., 2010; Phebus et al., 2011; Trainer et al., 2009) recent vacuum chamber experiments on deposition mode ice nucleation (direct vapor-to-ice phase transition) of H\(_2\)O in Mars atmospheric conditions. These studies found a clear temperature dependence of the contact parameter of water on mineral dust and Au/Si substrates, the dependence appearing linear or exponential depending on the temperature range of the experiments.

We calculate nucleation temperature as a function of partial pressure assuming a functional shape (linear, exponential, hyperbolic tangent) of \( m(T) \) in our nucleation model, and fit the data in the observational parameter space (temperature and vapor partial pressure). For each dataset we run several Markov chains corresponding to the possible \( m(T) \)-models.

CONCLUSIONS

We suggest one new (hyperbolic tangent) and test several \( m(T) \) dependencies (linear, exponential, hyperbolic tangent). Two of these (exponential and hyperbolic tangent) may be used to avoid unphysical behavior \( (m > 1) \) when \( m(T) \) is implemented in heterogeneous nucleation modeling. However, more measurements are required to fully constrain the \( m(T) \) dependencies. We show the importance of large temperature range datasets for constraining the asymptotic behavior of \( m(T) \), and we call for more experiments in a large temperature range with well-defined particle sizes or size distributions, for different IN types and nucleating vapors.

REFERENCES


Improved parameterization for H$_2$SO$_4$ - H$_2$O nucleation

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Keywords: homogeneous sulfuric acid - water nucleation, Classical Nucleation Theory, parameterization

INTRODUCTION

We are currently extending the two-component nucleation parameterization for sulphuric acid and water in stratospheric conditions (Vehkamäki et al., 2002) for a larger validity range. One motivation for doing this was the need for nucleation parameterizations for the atmosphere of Venus. Both the clouds of Venus and aerosols found in the Earth’s stratosphere are mainly composed of sulphuric acid droplets, and sulfuric acid nucleation has a role also in tropospheric particle formation.

METHODS

We use the thermodynamically consistent version of the Classical Nucleation Theory (Noppel et al., 2002). The previous model was improved by deriving analytical formulae for the second derivatives of the formation free energy, since the numerical derivatives were unstable at the one-component limit. Instead of the cluster distribution based on the dihydrate used previously, we have used the self-consistent distribution of (Wilemski and Wyslouzil, 1995), which behaves correctly at the one-component limit, and constrained it by scaling to recent quantum chemistry calculations (Kurtén et al., 2007). We have studied analytically the differences between the kinetic parts of the one- and two-component models, and verified that the numerical models behave as predicted by the analytical studies. In developing the parameterization, for continuity and consistency, the two-component model is used also at the one-component limit. When the critical cluster contains only one sulfuric acid molecule (or less), we use the kinetic particle formation equation. The parameterization is valid for the temperature range of 165-400 K, relative humidities ranging from 1e-6 to 100%, and sulphuric acid concentrations of $10^4$ - $10^{13}$ m$^{-3}$.

CONCLUSIONS

Parameterizations will be given for nucleation rate ($J > 10^{-1}$ m$^{-3}$s$^{-1}$), radius and composition of and number of molecules in the critical cluster. If the number of sulfuric acid molecules in the cluster is $\leq 1$, a simple kinetic regime formula for $J$ can be used. A parameterization for the threshold acid concentration for $J = 1$ cm$^{-3}$s$^{-1}$ is given as well. We recommend using the new model and the improved parameterization, once published, both for Terrestrial atmosphere studies and also for the Venus cloud community.

ACKNOWLEDGEMENTS

We wish to thank the Agence national de la recherche (ANR, project Exoclimats), the Programme national de planétologie (project ATMARVEN), the Solar System Group of Institut Pierre Simon Laplace, and the ERC - Starting MOCAPAF grant no. 57360 for funding.

REFERENCES


Application of the first nucleation theorem into cases with subcritical cluster loss

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Keywords: nucleation, kinetic nucleation theorem, losses, law of mass action

INTRODUCTION

During past years, the first nucleation theorem (FNT) has been widely used to assess the molecular mechanism of new particle formation (NPF). However, in a closer inspection it turns out that such analysis does not yield reliable results when NPF is taking place in inhomogeneous environment, for example in the atmosphere. (Kupiainen-Määttä et al., 2014) Recently, we have formulated an analytic theory to take account the effect of subcritical cluster losses on the FNT (Malila et al., 2014).

MAIN RESULTS

To derive the extensions of the kinetic first nucleation theorem into cases with subcritical cluster losses, we make only following assumptions:

— nucleation takes place via the Szilárd mechanisms, i.e. only monomer–cluster processes are considered; under such conditions all loss processes are linear with respect to the corresponding cluster concentration,

— metastable phase behaves as isothermal ideal vapour, and the law of mass action and condition of detailed balance hold for monomer–cluster processes.

It should be noted that the validity of these assumptions is not completely obvious when studying NPF in inhomogeneous systems (Kupiainen-Määttä et al., 2014). Sum rules for the formation rate $J_g$ of a $g$-mer [cluster containing $g$ monomers, (1)] and generalising the kinetic FNT (2), and also an asymptotic version of the FNT (3) now follow:

$$\sum_{g=1}^{G-1} P(g)J_g = J, \quad (1)$$

$$\sum_{g=1}^{G-1} \left( \frac{\partial \ln J_g}{\partial \ln S} \right)_{T, \langle q_g \rangle} - g \cdot P(g)J_g = J, \quad (2)$$

and

$$\left( \frac{\partial \ln J_g}{\partial \ln S} \right)_{T, \langle q_g \rangle} g \rightarrow g + 1. \quad (3)$$

Here $P(g)$ is the normalised distribution of growth rates of $g$-mers up to a large size $G$, $S$ is the saturation ratio, $J$ the corresponding, size-independent loss-free nucleation rate and $q_g$ the linear loss coefficient of a $g$-mer.

PROSPECTS AND CONCLUSIONS

Application of the sum rules (1) and (2) together with the condition of mass conservation shows that for clusters smaller than the (kinetic) critical size $\tilde{g}$, the formation rate $J_g \geq J$ and vice versa for $g > \tilde{g}$. Also the corresponding apparent critical size $\tilde{g}$ obtained from a naive application of the first nucleation theorem shows clear size dependence, being larger or equal to $\tilde{g}$, when the rate $J_g$ is observed at (or backcalculated to) large $g$, whereas for small $g$, $\tilde{g}$ approaches $g$ in accordance with Eq. (3).

Besides coagulation scavenging and wall/diffusion losses, formation of new particles via heterogeneous nucleation due to condensation of subcritical clusters on large organic vapour molecules (or other way round) can also formally be treated as a loss mechanism. In such case, application of FNT gives a path-weighted average over various possible NPF pathways, and it is possible to extend sum rules also for such cases. Furthermore, the asymptotic Eq. (3) together with potential heterogeneous pathway casts some doubt on the interpretation of particle size magnifier measurements at small nucleation rate.

We point out that our preliminary (2013) publication contained an error due to an erroneous assumption. Corrected derivations will be given in a forthcoming article (Malila et al., 2014).

ACKNOWLEDGEMENTS

This work was supported by the Finnish ACCC Doctoral Programme, the Academy of Finland through the Centre-of-Excellence Programme (decision no 272041), and the Atmospheric Systems Research (ASR) Program of the US Department of Energy.

REFERENCES


**Relationship between light absorbing carbonaceous particulate emissions and biomass combustion conditions**

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Keywords: Brown carbon, Burn phases, Biomass combustion, Wood stove

**INTRODUCTION**

Carbonaceous materials constitute a large fraction of the ambient aerosol. This fraction has a considerable effect on earth’s radiative balance by absorbing and scattering incoming solar radiation. Organic carbon (OC) is thought to have a cooling effect on the climate. However, it has been shown that the OC can be highly light absorbing in the UV-range (Kirchstetter et al., 2004), this fraction is often referred to as brown carbon (BrC).

Residential wood combustion (RWC) is a major source of BrC. However, there is poor knowledge about the relationship between combustion conditions and BrC emissions. For example, the impacts of stove operation parameters and the relationship to total OC emissions. Here we studied the optical properties and chemical composition of RWC emissions during different burn phases.

**METHODS**

Logs of birch were combusted in a conventional wood stove. Different phases of the burn cycle was injected into a steel chamber and then analyzed with a 7-wavelength aethalometer (model AE33). By assuming an absorption Ångström exponent (AAE) of 1.0 for black carbon (BC) we quantified the BrC emissions according to Sandradewi et al. (2008). Based on this approach we separate the total light absorbing carbon (LAC) into black carbon (BC) and brown carbon (BrC).

The composition of organic coatings and soot cores were investigated with a soot particle aerosol mass spectrometer (SP-AMS). The effects of intense photochemical processing on composition and optical properties were investigated by means of a potential aerosol mass reactor (PAM).

The fuel addition phase is the period shortly after adding fuel to a bed of ember, intermediate phase represents flaming combustion, and burn out phase was defined by a bed of glowing ember. The stove was operated in two modes: nominal burn rate (NB) and high burn rate (HB). A more intense combustion resulting from dryer fuel and a larger batch differentiated HB from NB, with HB being more intense than NB.

**CONCLUSIONS**

The BrC fraction of LAC is highly dependent on burn phases as shown in figure 1. During the fuel addition phases a considerable fraction (35-75 %) of the total absorption is due to BrC. During intermediate and burn out phases, BC dominates the total light absorption (85-95 %).

The mass absorption coefficient (MAC) for BrC was lower for the fuel addition experiments than other phases. Also, the AAE (370-660 nm) was significantly lower (~2.0) in the fuel addition compared to other phases (~1.0).

Emission factors of BrC and BC as well as PAHs were higher for HB than NB. Thus, excessive burn rates should be avoided.

![Figure 1. Ratio of BrC/LAC in the wavelength range 370 to 590 nm for different burning phases.](image)

**ACKNOWLEDGEMENTS**

This research was founded by the Swedish Research Councils FORMAS and VR.

**REFERENCES**


INTRODUCTION
The Arctic is a highly sensitive environment being affected more and faster than other parts of the world by Climate Change (AMAP, 2011). The Arctic is not easily accessible and field investigations are difficult to accomplish due to research infrastructure being almost absent. In this poster we present a newly build research station, Villum Research Station (VRS), at Station Nord in North Greenland (81° 36’N 16°39’ W). The station supports cross-disciplinary research in all aspects of environmental science.

STATION SET UP
VRS is a unique platform for cross-disciplinary research within the area of environmental science including exchange processes of the cryosphere and the atmosphere. It will consist of three platforms with state-of-the-art laboratory facilities and equipment. The three platforms can be operated simultaneously and independently.

Figure 1. New measurement building at VRS.

A Base Station located at Station Nord has already been build and consists of living quarters (10 scientist at a time), laboratories (chemistry, biology), storage rooms and a measurement building for atmospheric research as shown in Figure 1.

A Mobile Station will include mobile facilities as laboratories, living quarters consisting of tents and vehicles and mobile instruments. The Mobile Station will make it possible to conduct atmospheric, cryospheric, marine and geological research at locations in the vicinity of Station Nord. The Mobile Station will be up and running during 2015.

An Air Station will consist of instrumentation to conduct research with remote sensing techniques to investigate atmospheric parameters with vertical resolution. Additionally, Unmanned Aerial Vehicles and ground based remote sensors will support these investigations. The Air Station will be in operation from early 2016.

PRESENT AND FUTURE ATMOSPHERIC MEASUREMENTS
Table 1 provides a list of present and planned (beginning of 2015) atmospheric monitoring at VRS.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Parameter</th>
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<td>SMPS</td>
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<tr>
<td>OPC</td>
<td>Particle number size distribution &gt; 500 nm</td>
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<tr>
<td>MAAP BC concentration</td>
<td>Nephelometer Scattering coefficient (3 wavelengths)</td>
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<td>O3, GEM, NOx, CO, CO2, CH4, H2</td>
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<td>Filterpack Sampler</td>
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<td>High Volume Sampler</td>
<td>OC/EC concentration in PM10, POPs</td>
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<td>ACSM</td>
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ACKNOWLEDGEMENTS
This work was supported by Cryosphere-Atmosphere Interaction in a Changing Arctic Climate (CRAICC), the Arctic Monitoring and Assessment Programme (AMAP), the Arctic Research Centre (ARC) at Aarhus University and the Danish Villum Foundation.

REFERENCES
THE INCLUSION OF BROWN CARBON AEROSOLS IN THE ECHAM-HAMMOZ AEROSOL-CLIMATE MODEL

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Keywords: climate modeling, remote sensing, aerosols, brown carbon

INTRODUCTION

One of the key aspects in climate change is the effect of atmospheric aerosol particles on solar radiation. For black carbon (BC) and brown carbon (BrC), commonly referred as light-absorbing carbonaceous aerosols (LAC), the climate effects are complex. To estimate the overall climate effect of LAC, the level of aging and the distribution of LAC in horizontal and vertical have to be known.

Most climate models do not include BrC because its importance on radiative transfer has only recently been realized. BrC is emitted into the atmosphere from incomplete combustion and it is formed in the atmosphere as secondary organic aerosols. Consequently, the optical properties and the emissions of atmospheric BrC aerosols are not well known and their estimates have been based on theoretical studies and laboratory measurements (Feng et al., 2013). In order to make proper estimates on the climate effects of LAC, optical properties and emissions of BrC have to be modeled adequately.

METHODS

Feng et al., (2013) estimated that 66 % of the total organic matter from biofuel and biomass burning emissions is BrC. In our model comparisons with Aerosol Robotic Network (AERONET) data this emission factor did not produce good agreement on atmospheric burdens of BrC. Therefore, the aim of this research is to produce new measurement based estimates for BrC emissions. We use retrievals of atmospheric BrC concentrations to estimate the fraction of BrC emissions from the total organic carbon (OC) emissions. This is done using an iteration tool based on an Extended Kalman filter. With the combination of measurement data and inverse problem methods we can optimize the BrC emission fractions for different emissions sources (biomass burning, fossil fuel, and biogenic emissions) in the ECHAM-HAMMOZ model. This optimization produces the best match between the modeled and retrieved BrC concentrations in the atmosphere.

The measurement data used in this research is from AERONET which uses Cimel sun photometers which measure columnar aerosol optical depth (AOD) spectrally. AERONET also provides the angular distribution of sky radiances and aerosol properties such as aerosol size distribution, complex refractive index, and single scattering albedo. The atmospheric BrC concentrations are retrieved from the complex refractive index data (Schuster et al., 2005).

The aerosol-climate model used in this project, ECHAM-HAMMOZ, describes all known relevant atmospheric aerosol processes: emissions, removal, aerosol microphysics, chemistry, radiative effects, and aerosol-cloud interactions. It includes the main atmospheric aerosol compounds: sulphate, organic/black/brown carbon, sea salt and mineral dust. ECHAM-HAMMOZ model escribes the aerosol size distribution using either a modal or a sectional approach. The model meteorology is nudged towards reanalysis data.

CONCLUSIONS

In order to quantify how much BrC is emitted to the atmosphere we have developed a tool for optimizing BrC emissions in climate models using retrieval data available from AERONET. We have tested the tool with synthetic data and the optimization performed well. Furthermore, the first results with measurement data look promising. However, we still have to improve the tool before new measurement based estimates for BrC emissions can be provided.

ACKNOWLEDGEMENTS

This work was supported by the Academy of Finland under grant no. 272041.

REFERENCES

Feng, Y et al. (2013), Atmos. Chem. Phys., 13, 8607-8621.
Structure of “multi-layer graphene-carbon nanoflower” composite

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Keywords: multi-layer graphene, carbon nanoflower, carbon-carbon composite

INTRODUCTION

Composites of different carbon nanostructures have been studied extensively during the past years because their combination may result in more efficient materials for, e.g., lithium-ion batteries. The features of the fabricated composites, may affect the electrical, optical and mechanical properties of the materials. Therefore, it is important to examine the structure of the composites to find out the most feasible application areas.

The synthesis of a “multi-layer graphene-carbon nanoflower” composite (MLG/CNF) (Fig. 1a) is previously reported (Miettinen et al., 2014). Here, structure of the composite was studied (Miettinen et al., under review).

METHODS

Aberration corrected high-resolution transmission electron microscope (TEM, JEOL JEM-2200FS) was used. The analyses were performed at electron acceleration voltage of 80 kV. Selected area diffraction analysis (SAED) was performed from the MLG sheets.

Raman spectroscopic analyses were done with two confocal setups, a Jobin-Yvon LabRAM HR Evolution equipped with a 405-nm SureLock solid state laser and a 632.8-nm He-Ne laser and a Jobin-Yvon LabRAM HR using the 482.5-nm line of a Coherent Kr⁺-ion laser.

RESULTS AND CONCLUSIONS

SAED and Raman analyses showed that graphene layers were rotated to each other. The most common rotation angle in the MLG sheets based on SAED analysis was 30 ± 2° (Fig. 1b). Raman analysis designated the rotation angle of 11-12°. The discrepancy indicates that the rotation angle in the CNFs and the wrinkled regions of the sheets has to be smaller than 30°.

Both folded and free standing, unfolded edges were present in the sheets. The free standing edges were usually rough and no preferred chirality was found. Overlapping boundary interfaces were dominant between the graphene domains.

Figure 1. TEM images of the MLG/CNF composite (a) and a CNF (c), b) SAED pattern from the area marked with circle in (a), and d) a higher magnification image of a cavity in a CNF.

Due to rotational faults the interlayer distance in the sheets was increased ~12 % compared with graphite. The CNFs (Fig. 1c) contained nanosize cavities (Fig 1d).

Rough edges and overlapping boundary interfaces may degrade the electronic properties of the composite from the ideal values. However, the wrinkled network of the MLG sheets and the CNFs may increase, e.g., lithium-ion insertion capacity of the composite.

ACKNOWLEDGEMENTS

This work was supported by the strategic funding of the University of Eastern Finland (NAMBER) and by the funding from the Finnish Funding Agency for Technology and Innovation (TEKES) under ScaleG project (grant number 70014/13). This work made use of Aalto University Nanomicroscopy Center (Espoo, Finland) and Paul-Drude-Institut für Festkörperelektronik (Berlin, Germany) facilities.

REFERENCES

Nonlinear proxy function for atmospheric hydroxyl radical concentration

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Keywords: OH concentration, proxy, statistical prediction, atmospheric modelling

INTRODUCTION

The goal of our study is to build a statistical model which is able to predict the hydroxyl radical (OH) formation by using the information about solar radiation and atmospheric sinks of OH. OH is the most important chemical cleaning agent of the atmosphere (Levy, 1971; Rohrer and Berresheim, 2006). It determines the oxidizing power of the atmosphere, and thereby controls the removal of nearly all gaseous atmospheric pollutants. The problem is that hydroxyl radical concentration is difficult to measure and in many measurement sites no OH data are available. Rohrer &Berresheim (2006) showed that OH production can be defined as a function of J(O³D) which, however, is also rarely available in atmospheric models and in measurement datasets.

METHODS

Rohrer and Berresheim (2006) presented an equation for approximating OH concentration by using nonlinear function of photolysis frequency of ozone J(O³D) as a predictor. However, J(O³D) is rarely available in atmospheric models and in measurement datasets. The proxy was given by

\[ [OH] = a \cdot J(O³D)^b + c \]

where the exponent \( b \) reflects the combined effects of all photolytic processes which generate OH either directly or via production of and recycling from HO₂. The dependence of OH on reactants such as NOx, hydrocarbons, O₃ or H₂O is condensed into the single pre-exponential coefficient, \( a \). The coefficient \( c \) includes all processes that are light-independent. Berresheim et al. (2013) found out that the OH-J(O³D) relationship is highly dependent on NO level and thus it will be one of the new predictors tested in our proxy.

The analysis will be done by using variables which are commonly measured in different sites and can be easily accessed with atmospheric models, as Mikkonen et al. (2011) did for H₂SO₄ concentration proxy. Atmospheric OH is mainly produced by photochemistry either directly or recycling from HO₂, thus we can estimate the daytime production of OH with solar radiation and some correction factor taking account possible cloudiness. We will use global radiation as the main predictor instead of J(O³D) because it is more commonly available in different datasets and the correlation between these two variables is evident. We will then decompose the terms \( a \) and \( c \) by using other measured variables such as O₃, RH, and NOx resulting proxies which can be used to predict [OH] in different environments. Especially parameterization of the \( c \) term improves the estimation ability of the proxy in low radiation periods.

Figure 1. Prediction with the test proxy

The new proxy can be written in form

\[ [OH] = a \cdot [Radiation]^b \cdot [VarX]^c + d \]

where \( [Radiation] \) refers to global radiation, \( [VarX] \) represents a combination of measured atmospheric variables affecting to \([OH]\) and \( a, b, c \) and \( d \) are coefficients estimated from the measurement data. In Pietikäinen et al. (2014) we used the simplest version of the proxy with \( [VarX] \) being a constant. For the result shown in Figure 2, parameters were defined such that \( [VarX]=f([NO] \cdot [O_3]) \), \( b \) is exponent near to unity, and \( d=f([NO_2] \cdot [O_3]) \). RH may also act as an indicator of loss process of \([OH]\)in either of the terms. More precise functional form will be confirmed with subsequent analysis taking carefully account the results of Berresheim et al. (2013).

Our results are preliminary but highly promising. The analysis will continue and the results will be confirmed with data collected from multiple other sites.

ACKNOWLEDGEMENTS

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REFERENCES

Boreal forest ecosystem oxidation capacity: first ever modelled reactivities of O$_3$ and NO$_3$

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Keywords: oxidation, reactivity, boreal forests, boundary layer mixing

INTRODUCTION

Boreal forests are a great source of a vast amount of biogenic volatile organic compounds (BVOCs). Carbon, as part of different BVOCs, is usually emitted in a rather reduced oxidation state from the biosphere into the atmosphere. During its stay in the atmosphere carbon (as part of the BVOCs) gets into contact with oxidants that are continuously increasing its oxidation state. New products are formed that have different chemical and physical properties. These compounds often have lower vapour pressures than the parent molecule and can have the potential to participate in aerosol formation and growth, and in production of cloud condensation nuclei (CCN) and thereby affect the climate (Makkonen et al., 2012). At present, researchers have only investigated the reactivity of the atmospheric cleaning agent; OH. However, there exists other atmospheric oxidants too that have the potential to be important.

METHODS

In order to investigate the boundary layer oxidation capacity in the boreal forest ecosystem we use the 1D chemical–transport model SOSAA (Boy et al., 2011). Thereby we are also able of investigating the vertical importance. SOSAA includes modules for boundary layer meteorology (SCADIS), biogenic canopy emissions (MEGAN), gas phase chemical mechanistics (MCM) and aerosol dynamics (UHMA).

Our location of choice is the SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relations), Hyytiälä, Southern Finland (Hari and Kulmala, 2005), which is very well characterised and located in the boreal forest zone.

We focus on the time period from 12 July – 12 August 2010 where the HUMPPA-COPEC-10 campaign (Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry 2010) took place.

CONCLUSIONS

For the very first we model the reactivity of other oxidants (O$_3$ and NO$_3$) than OH together with the reactivity of OH. We investigate their vertical profile and their reactivity towards specific groups of compounds. We also compare the measured OH-reactivity to the modelled and discuss the missing and unexplained fraction of the reactivity. Further we introduce the concept of ”oxidative strength”, which not only takes the reactivity of the oxidant into account, but also its concentration. Thereby we are able to evaluate which specific oxidant is capable of cleaning the atmosphere for the largest volume of pollutants. By doing this, we are able to map the most effective oxidant at the SMEAR II station as a function of time. We conclude that O$_3$ is at all times the oxidant that is capable of removing most compounds from the atmosphere, however it is also the oxidant that is most selective; meaning it can only remove a quite small amount of different species compared to NO$_3$ and OH. During night time, the oxidative strength of NO$_3$ is about twice that of OH, while OH dominates the oxidative strength of NO$_3$ during light hours.

Connected to the discussion of the ability of the oxidants is also their lifetime. We present the first boreal forest calculated lifetimes of NO$_3$ based on measurements.

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Respiratory tract deposition of inhaled wood smoke particle in healthy volunteers and patients with chronic obstructive pulmonary disease

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Background
Respiratory deposition of air pollution particles in the lungs is important as these particles are strongly linked with adverse health effects. This study was aimed to determine the size-resolved deposition fraction (DF) of sooty wood smoke particles in the lungs of healthy subjects and patients with chronic obstructive pulmonary disease (COPD).

Methods
12 healthy and 5 COPD subjects inhaled diluted wood smoke from incomplete soot-rich combustion in a common wood stove. The DF of smoke particles (10-500 nm) was measured during three 15-min exposures in each subject during spontaneous breathing using Respiratory Particle Deposition Instrument (RESPI) technique. Lung function was measured using standard spirometry.

Results
DF in healthy subjects and COPD patients in the particle size range of 10-500nm was 32% and 35% respectively. This can be compared with DF of 21-23% during previous wood pellet combustion experiments. For particle mass, the total DFs found in this study were 0.22 ± 0.06 for healthy subjects and 0.30 ± 0.15 for COPD patients. DF and breathing frequency were negatively correlated (p < 0.01).

Conclusions
The DF of the investigated sooty wood smoke particles was higher than the previously investigated particles generated by other wood smoke combustion processes. Together with toxicological studies, which have indicated that incomplete biomass combustion particles rich in soot and poly-aromatic hydrocarbon (PAHs), are especially harmful, these data highlight the health risks of inadequate wood combustion. The tendency towards an increased DF in COPD patients may contribute to more severe health effects for this group.
Effects Of Experimental Wood Smoke Exposure In Healthy Human Subjects

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Background
Indoor smoke from combustion of solid biomass fuel is a major risk factor for respiratory disease worldwide as concluded by WHO. Epidemiological studies have indicated adverse effects on obstructive airway diseases, acute lower respiratory tract infections and tuberculosis. The mechanisms by which wood smoke exhibits its effects on human health are not well understood. The aim of this study was to determine whether exposure to wood smoke produced from incomplete combustion would elicit an airway inflammatory response.

Methods
Fourteen healthy subjects underwent controlled chamber exposure on two occasions to filtered air and to sooty wood smoke (PM1 ~ 314 μg/m³), generated by a common Swedish wood stove firing birch logs. The study was performed in a double-blind randomized cross-over fashion and the subjects alternated between exercise (Ve=20 L/min/m²) and rest at 15-minute intervals for 3 hours. Bronchoscopies with endobronchial biopsies taking were performed 24 hours after each exposure. Bronchial mucosal biopsies were analyzed using immunohistochemistry.

Results
There was a significant increase in submucosal and epithelial CD3+ lymphocytes (p<0.01 and <0.05 respectively), together with CD8+ cells in the epithelium (p<0.05) after exposure to wood smoke compared to filtered air. Mast cells were also significantly increased in the submucosa (p<0.01), meanwhile, there were no significant changes in other cell types or adhesion molecule expression after exposure to wood smoke.

Conclusions
Wood smoke exposure caused a significant increase in bronchial epithelial and submucosal CD3+ lymphocytes together with an increase in mucosal mast cells. Further examination revealed a significant increase in CD8+ lymphocytes within the epithelium. Unexpectedly there were no indications of any neutrophilic airway response or recruitment of alveolar macrophages. Further research is needed to determine the precise role of these events in relationship to the adverse health effects attributed to wood smoke exposure.
Atmospheric dilution and dispersion of particles and SO$_2$ emitted by a coal fired power plant

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Keywords: coal combustion, power plant emission, dispersion, dilution

INTRODUCTION

Coal provides 40% of world’s electricity needs (IEA 2014). Only few studies present sparse data from power plant flue gas plumes (Stevens et al. 2012, Brock et al. 2002). Brock et al. sampled the flue gas into the instruments installed into the aircraft and studied particle sizes larger than 40 nm when the plume age varied between very fresh to 10 hours. Stevens et al. measured the cross-wind particle number size distribution and gas concentrations different distances but presents the results 36 km away from the power plant and implemented those results to their computational model. Normally, the flue gas emissions are measured from the stack and implemented to dilution models, but in this study the flue gas concentrations were measured directly from the atmosphere during the dilution process. Results are used to evaluate the air quality near power plant.

METHODS

Measurements were made from helicopter which was equipped with CPC3776 (TSI Inc), gas analyzers for CO$_2$, CH$_4$, H$_2$O, and SO$_2$ (Cavity spring-down spectrometry Picarro model G1301-m CO$_2$/CH$_4$/H$_2$O Flight Analyzer and Thermo Scientific Inc. model 43i SO$_2$ analyzer) and EEPS (TSI Inc) to measure the particle number size distribution. The helicopter flew two times in a day measuring different flue gas cleaning situations during coal combustion. Firstly only electrostatic precipitator (ESP) were used for the flue gas cleaning and, secondly, the flue gas was cleaned with ESP, desulphurisation plant (DSP) and fabric filters (FF). The flue gas sample was taken headwind and downwind of the flue gas plume avoiding mixing the helicopter exhaust to the flue gas plume. In addition to helicopter measurements, the same situations were also measured at the stack. The sample was taken with Fine particle sampler (FPS, Dekati Inc) and the particle number size distribution was measured by ELPI (Dekati Inc) and the total particle number concentration by CPC3776 (TSI Inc.).

CONCLUSIONS

According to preliminary results, the maximum particle number concentration of the flue gas plume was around 2·10$^4$ cm$^{-3}$ measured from the helicopter with CPC when both the DSP and the FF were bypassed. In 200 s the number concentration reached the background level. Nearly similar trends were measured also for SO$_2$ and CO$_2$. The DSP and the FF decreased significantly the particle number and SO$_2$ concentrations in the plume. In comparison, the total particle concentration at Helsinki city centre are around 2.2-4.6·10$^4$ cm$^{-3}$ (Lähde et al. 2014) in a high traffic flow streets being thus even higher than the maximum flue gas plume total particle number concentrations observed at 110 meters above sea level.

Figure 1.Total particle number, SO$_2$ (ppb) and CO$_2$ (ppm) concentrations as a function of plume age measured from helicopter with CPC3776 when the DSP and the FF of the power plant were bypassed.

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Probing the organic fraction of nascent sea spray aerosol using volatility

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Keywords: volatility, sea spray aerosol, organic enrichment, surfactants

INTRODUCTION

Under windy conditions breaking waves entrain air bubbles in seawater. These bubbles rise to the surface and when they burst, sea spray aerosol is released into the atmosphere. Sea spray aerosol has been shown not only to contain inorganic sea salt but also organic matter scavenged from the surrounding seawater, and the sea surface microlayer in particular (Qnn et al., 2014). It has been suggested that this organic fraction may dominate in the sub-micron aerosol size range of sea spray aerosol (de Leeuw et al., 2011). A laboratory study by Modini et al. (2010) indicated that natural seawaters contain some organic fraction. This was probed based on their volatility. However, the type of compounds that could contribute significantly to organic enrichment in sea spray aerosol and the degree of enrichment remains largely unsolved. In this work, a study of the volatility of laboratory generated sea-spray aerosol is presented. Aerosol particles were generated from artificial sea water and artificial seawater doped with different organic model compounds. The organic model compounds studied covered a range of surface activities: from low to strong.

METHODS

A Volatility-Tandem Differential Mobility Analyser (VTDMA) system setup was employed, which can be used to determine the size-resolved volatile fraction of an aerosol population (Wehner et al., 2002). Particles were generated from bubble bursting in a sea spray tank (10 L) using a plunging jet (King et al., 2012), dried and subsequently size-selected using the first DMA. Collected particles were led through a thermodenuder at varying temperatures (25-400°C). In the thermodenuder, volatile aerosol components are removed by heating and subsequent denuding using activated charcoal. Finally the size distribution was measured using a Scanning Mobility Particle Sizer (SMPS) system without a neutralizer.

The so-called Volume Fraction Remaining (VFR) was determined using the following equation.

\[ VFR = \frac{V_f}{V_i} = \frac{D_f^3}{D_i^3} \]

where Vi and Di are the original volumes and diameters of particles measured by bypassing the thermodenuder; Vf and Df are the volumes and diameters of the particles after passage through the thermodenuder at a given temperature. VFR was determined for particles of selected initial sizes (35 nm, 65 nm and 100 nm respectively).

CONCLUSIONS

Our preliminary results shows that it is possible to observe organic enrichment in the generated artificial sea spray particles based on the volatility curves from concentrations of organics in the sea spray tank as small as 0.5 mg L⁻¹ organic in 10 L solution (containing 100 g of NaCl).

The magnitude of the observed enrichment was however also dependent on the organic compound used. Fulvic acid, which is surface active, showed an enrichment effect of 30 -80 by volume relative to concentration of bulk solution, while sucrose, which is a non-surfactant compound, did not show any enrichment effect. Sodium laurate, which is a non-ionic surfactant commonly used in colloidal chemistry was also probed.

Our observations indicate that surfactants may contribute significantly to sea spray aerosol. In particular, the observed enrichment effect of fulvic acid, which could be a major component of dissolved organic matter in seawater and also terrestrial runoff (Thurman, 1985) could be of importance. In the long run, it is planned to target, identify and quantify surface-active compounds such as humic substances, lipids and fatty acids in real seawater samples using other support analytical techniques including Mass Spectrometry. Concurrent measurement of volatility and characterization of surface-active compounds would contribute to the currently poor understanding of atmospheric organics originating from seawater.

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Predictions of atmospheric particle formation probability in Hyytiälä, Finland

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Keywords: new particle formation, forecasts, airborne measurements

INTRODUCTION

Atmospheric new particle formation (NPF) events are observed in many environments in the boundary layer (e.g. Kulmala et al., 2004). The majority of these observations are made using stationary ground-level instrumentation. To obtain information on the spatial extent of NPF events both in the vertical and horizontal directions, measurements using aircrafts are needed. As part of PEGASOS project, a Zeppelin NT airship was performing aerosol, trace gas and photochemistry measurement flights in Central Finland during May–June 2013. For optimizing the use of flight hours, forecasts of probability of NPF events in the coming days were prepared.

METHODS

The purpose of the NPF forecasts was to predict the probability of NPF events during the next three days at the SMEAR II station area, in order to have enough time for preparing the measurement instruments needed on different flights. The final NPF forecast was always given for the next day.

Concentrations of SO2, O3, NOx, CO and OH, particulate matter (PM10) and relative humidity were obtained from the SILAM air quality model developed by the Finnish Meteorological Institute. This model provides air-quality predictions for the next 5 days over Scandinavia, and is freely accessible (http://silam.fmi.fi/). For the purposes of our NPF event forecasts, we used predictions for the ground level during next 3 days from the model grid point nearest to Hyytiälä (61°51'N, 24°17'E).

The source areas and arrival routes of air-masses were forecasted for 96 hours prior to their arrival at Hyytiälä using the HYSPLIT model with Global Forecasting System (GFS) weather forecast data. We also used several weather forecasts available on the internet (including Finnish Meteorological Institute and Foreca) to evaluate the probabilities of cloudiness and rain.

RESULTS AND CONCLUSIONS

The PEGASOS-Zeppelin Northern mission took place 3.5.–11.6.2013. Early in the campaign several strong NPF bursts occurred, and our forecasts were able to capture these as well as the days when no particle formation occurred. During this time air masses were originating mainly from the Atlantic, and arriving to Hyytiälä over Scandinavia. On some days the air was remarkably clean, characterized by very low SO2 concentration (<0.1 ppb), resulting in low sulphuric acid concentration and weak or no NPF even at clear-sky conditions.

After mid-May until early June the airmasses arrived to Hyytiälä mainly from east, either spending several days over continental Russia or in some cases more directly from Arctic Ocean via northwest Russia. This rather unusual airmass transport pattern to Hyytiälä made the NPF forecasting more challenging. During this time there were situations when the polluted airmasses resulted in high condensation sink preventing NPF occurrence. Also SILAM forecasts for SO2 and PM10 concentrations were less accurate during the easterly airmasses compared to when airmasses came from west or south.

During the 40 day campaign we predicted NPF to occur on 8 days, and during 7 of these an NPF event occurring over several hours was observed. On none of the days forecasted to be non-NPF days was there appearance and growth of new nucleation mode particles. Main challenge in predicting the NPF occurrence was to obtain as reliable as possible input data from SILAM, HYSPLIT and weather forecasts. The approach and methods described here can most likely also be applied to other locations where there is sufficiently long observations available characterizing the ambient conditions in which NPF occurs.

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REFERENCES

A novel set-up for source characterization and human exposures of biomass combustion aerosols

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Keywords: biomass combustion, aerosol chamber, controlled human exposure, health effects

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Emissions from biomass combustion are a major source of indoor and outdoor air pollution, and are estimated to cause millions of premature deaths worldwide annually. Pollution from different biomass combustion sources are a complex and varying mixture of gases and particles, strongly dependent on fuel, technology and operation [Kocbach et al., 2009]. Although adverse respiratory effects have been associated with "wood smoke" in epidemiological and controlled exposure studies, important information concerning biomass combustion aerosols is still missing. Examples of such areas are; cardiovascular effects, underlying biological pathways and importance of different aerosol particle properties. A chamber set-up built for controlled human exposures gives unique opportunities to directly relate specific exposure conditions to different short term (acute) respiratory and cardiovascular responses in humans.

The objective of this project was therefore to describe and evaluate a novel chamber set-up for studies of health effects of biomass combustion aerosols using controlled human exposures. In this paper we discuss the biomass combustion aerosol exposure set-up including aspects of; i) combustion systems, ii) aerosol dilution, iii) chamber design and function, and iv) exposure data from the first recently performed campaign.

The exposure set-up is located in connection to the combustion laboratory within the Thermochemical Energy Conversion Laboratory (TEC-Lab) at Umeå University. The facility includes several combustion technologies to be used for different aerosol generation purposes such as human exposures and/or other aerosol experimental research. For example, traditional wood log stoves, modern wood pellet boilers using different burner technologies, a fluidized bed reactor and novel grate fired reactors for controlled generation of different kinds of biomass aerosols, are available.

Different flue gas/aerosol dilution systems are available, e.g. ejector dilutors (ED) and porous tube dilutors (PTD). In the first exposure campaign, a three step dilution system with filtered air at ambient temperature was used including a first PTD (4:10), followed by an ED (4:6) and a final counter-current flow injection in the main HEPA filtered air flow that enters the chamber.

The chamber is 15.3 m³ (2.7 x 2.4 x 2.4 m) with a small ante-chamber with interior surfaces made of stainless steel/aluminium, except for 2.4 m² observation glass window facing a control room. The set-up is designed for air exchange rates of 2-10 times per hour. CO, NOx, and total hydrocarbons as well as temperature and relative humidity are continuously monitored. Particle mass concentration is measured by a TEOM equipped with a PM1 pre-cyclone and an integrated filter sampler. Particle mobility size distribution and number concentration are measured with a SMPS system. In addition, several different filter and impactor sampling lines are applied for off-line chemical characterization including, e.g. carbon fractions (OC/EC), PAH/oxyl-PAH and inorganic alkalies and trace metals, as well as toxicological (in-vitro) characterization.

A first human exposure study in the new set-up was performed to elucidate acute airway inflammatory responses and cardiovascular effects after exposure to emissions from incomplete wood log combustion. A common Nordic wood stove was used with a special adjusted combustion approach to generate incomplete (soot-rich) conditions in a repeatable manner for the exposure campaign. The target PM10 mass concentration in the chamber was 300 μg/m³ thus in line with a previous experimental wood smoke study [Sehlstedt et al., 2011] and several diesel engine exhaust studies performed by the Umeå group and collaborators.

Fourteen healthy non-smoking subjects were successfully exposed to diluted wood smoke (PM10: 314±38 μg/m³) or filtered air for three hours in a randomized, double-blind crossover study. The EC/TC (total carbon) ratio was 0.72 ± 0.08, a nd it was estimated that the total PM consisted of approximately 38% soot, 24% organics and 38% inorganics.

Aspects of chamber function (e.g. flow profiles and mixing conditions) as well as aerosol dynamic effects (e.g. coagulation and wall losses) at different chamber conditions are presently under evaluation and will be discussed. Accordingly, the new and novel set-up for biomass combustion aerosol generation, characterization and health effect studies has successfully been established and so far used in two human exposure study and one aerosol ageing and toxicology study.

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Properties of biodiesel exhaust particles from two non-road engines

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Keywords: biodiesel, exhaust particles, physicochemical properties, PAH

During the last decades there has been a global drive towards finding sustainable and clean bio-based alternative fuels for the transport sector. Currently, biodiesel represents one of the most established liquid biofuels on the international market. Biodiesel is composed of fatty acid methyl esters which can be used alone, or blended with petrodiesel in any proportions. Whilst there is an obvious positive climate related impact of replacing fossil fuels with renewables, it is also important to assess the overall environmental health effects in different future scenarios. Generally, there is still very little information available on this issue, and for biodiesel some emission studies have focused on mutagenic effects [Bunger et al, 2007]. However, very little is still known about the detailed properties of exhaust particles from biodiesel and other biofuels [Swanson et al, 2007]. The objective of this work was therefore to investigate the physicochemical and oxidative properties of biodiesel exhaust particles from two engines (one old and one new) and compare these properties to particles from standard diesel exhaust.

The experimental setup was composed of two different engines; one older engine produced from 1996 to 2004 that meets EU Stage I and Tier 1 for non-road, and one newer engine in production from 2011 with emission class EU Stage 3B and EPA Tier 4i for non-road with diesel particulate filter (DPF). The engines were connected to an engine dynamometer and running under control of a computer program according to the European Transient Cycle (ETC) or at idling conditions. Three different fuels were tested; 100wt% standard diesel (SD), a blend of 30wt% RME biodiesel with 70wt% SD, and 100% RME biodiesel. Sampling was performed during a modified ETC cycle, including only a 10 min city period as well as three steady state points, i.e. max load, max torque and idling.

Particle mobility size distribution and number concentration were measured with a differential mobility spectrometer (DMS500, Cambustion). In addition, several filter sampling lines were applied for off-line mass concentration measurements and chemical characterization including, e.g. carbon fractions, PAH/oxy-PAH and trace metals. In addition, particles were sampled by a 5-stage impactor for determination of their oxidative properties using a synthetic human respiratory tract lining fluid model. The analysis determine the particles ability to consume the antioxidants ascorbate, urate and glutathione.

A clear difference in particle size distribution were seen in the old engine for the different driving modes although with rather similar trends between the different fuels (Fig 1). During transient engine load, a difference in the relation between the modes around 10 nm and 100 nm were seen between SD and B100. Further, considerably lower particle emissions were seen for the new engine compared to the old engine for all three fuels/blends tested, especially as the DPF filter reduced almost all particles. In the case of the new engine with DPF, no particulate filter sampling was possible. So far the results illustrate interesting differences in the exhaust particle size distribution for the different engines, driving conditions and fuels used, including biodiesel blends.

![Figure 1. Particle number size distributions for the old engine under idling and urban driving cycle running conditions.](image)

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Modelling particle distribution using combined power-law and log-normal distribution model

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Keywords: modelling, power-law, log-normal, sectional

INTRODUCTION

During the initial steps of aerosol evolution, e.g., in atmosphere or in exhaust plume, particle nucleation can occur simultaneously with particle growth by condensation and coagulation. Simultaneous nucleation and growth cause concentration to remain in the smallest particle sizes (Fig. 1. (a)), although growth transfers particles to larger sizes.

Particle dynamics modelling has previously been done using both sectional and log-normal (LN) approach (Sihto \textit{et al}., 2009; Wang \textit{et al}., 2012). Sectional method with sufficient amount of size sections is typically the most accurate in maintaining a realistic size distribution. Conversely, LN presentation approximates the distribution as log-normal; and therefore, it is not as accurate as the sectional model. However, LN model requires shorter computation time and less memory usage, which until now has been the best choice in simulations where particle dynamics is to be computed in a large number of computation cells, e.g., in CFD-simulation done in 3-D.

In the case of simultaneous nucleation and growth, LN presentation fails to maintain the realistic size distribution (Fig. 1), thus the average particle size and the width of the distribution are modelled inaccurate. Additionally, the rates of, e.g., deposition and coagulation are calculated in slightly wrong size range. Here we present a method to approximate the particle distribution as combined power-law (PL) and LN distribution (PL+LN).

SIMULATIONS

In the case of constant nucleation and growth rate without any other processes, particle distribution in the smallest sizes is the form of a power-law function. This can be seen from Fig. 1. (a), which represents the particle size distribution after 0.5 seconds of constant nucleation and condensation rate computed by different methods.

PL+LN model is basically a method where the size distribution is modelled as two modes (PL and LN), which both have 3 parameters. Therefore, the total distribution requires only 6 variables to be modelled, which is significantly less than in sectional model (usually hundreds of size sections, here 1000). In PL+LN model, nucleation forms particles to the smallest particle size of PL distribution, and coagulation transfers particles from PL distribution to LN distribution.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Particle distribution modelled as LN, sectional, and PL+LN distribution. (a) Simultaneous nucleation and condensation during the first 0.5 s. (b) Coagulation during the next 0.5 s.}
\end{figure}

Distributions in Fig. 1. (b) are the case when nucleation and condensation are switched off after the case in Fig. 1. (a), but coagulation has been affected the next 0.5 seconds. It can be seen that PL+LN method produces better shape for the distribution compared to LN method in both cases.

CONCLUSIONS

Combined power-law and log-normal particle size distribution model (PL+LN) is computationally efficient model that can be used to increase accuracy in modelling size distribution in case of simultaneous particle nucleation and growth compared to log-normal model. The main advantage of the model is obtained especially in CFD- and 3-D-simulations.

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A HYGROSCOPICITY CLOSURE STUDY COUPLED WITH MEASUREMENTS OF CHEMICAL COMPOSITION AND PHYSICAL PHASE STATE OF AMBIENT AEROSOLS IN THE SOUTHEASTERN UNITED STATES

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Keywords: hygroscopicity, SOA, phase state, SOAS

INTRODUCTION

Recent work has focused extensively on the closure between particle hygroscopic behaviour at sub-saturated conditions and cloud activity at super-saturated conditions (Prenni et al., 2007; Wex et al., 2009; Hersey et al., 2013). Recent results show that Secondary Organic Aerosol (SOA) derived from biogenic volatile organic compounds in the atmosphere (Virtanen et al., 2010) and from biogenic or anthropogenic precursors in the laboratory (Saukko et al., 2012; Pajunoja et al., 2014b) can exist as amorphous solids. We have also seen evidence that the hygroscopic behaviour of SOA at sub- and super-saturated conditions can be closely related to its physical phase state, oxidative state, and chemical composition (Pajunoja et al., 2014a). In addition to data already collected at a monoterpenes-dominated boreal forest site in Hyytiäjä, Finland, we aim to investigate these parameters in the Southeastern United States atmosphere, which is influenced by high biogenic emissions of isoprene from a temperate forest. This study is in line with several major science objectives of the Southern Oxidant and Aerosol Study (SOAS) near Centerville, Alabama, which is to understand the relationship between SOA composition and climate-relevant aerosol properties like hygroscopicity, cloud activity, and light extinction. During the SOAS field campaign (June-July 2013), simultaneous measurements of aerosol hygroscopicity under sub- and super-saturated conditions, aerosol composition, and particle phase state were made.

METHODS

Sub-saturated hygroscopic growth measurements were made with a Hygroscopicity Tandem Differential Mobility Analyser (HTDMA) in parallel with Cloud Condensation Nuclei counter (CCNc) activity measurements. We attempt to investigate in real-time the closure between the hygroscopicity parameters derived from the HTDMA ($\kappa_{\text{HTDMA}}$) and the CCNc ($\kappa_{\text{CCNc}}$) measurements while the Aerosol Bounce Instrument (ABI) was deployed at the SOAS supersite to investigate the physical phase state of ambient aerosols, and chemical composition of PM1 was obtained from an Aerodyne Aerosol Mass Spectrometer (AMS).

CONCLUSIONS

Preliminary data have shown that the $\kappa_{\text{HTDMA}}$ to $\kappa_{\text{CCNc}}$-ratio exhibits strong diurnal behaviour, which could be linked to diurnal variations in chemical composition, atmospheric aging and physical properties of SOA particles. Moreover, bounciness of the SOA particles is relatively high over the campaign except few days with higher inorganic fraction indicating mainly solid like organic fraction of the particles.

ACKNOWLEDGEMENTS

This research has been supported by Academy of Finland (272041, 259005, 267514, 139656), European Research Council (ERC Starting Grant 335478 and 278277 and Advanced Grant 227463)

REFERENCES


Modelling 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, including their phase. Formation of ice clouds, in particular, is not well understood. Ice crystals may form 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. We are using parallel molecular dynamics (MD) simulations to study heterogeneous nucleation of ice, looking at kinetic and thermodynamic factors controlling nucleation at different conditions and in the presence of different surfaces representing aerosol particles.

METHODS

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 & 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. 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 code (Todorov et al., 2006) 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 that are experimentally found to be active in heterogeneous nucleation.

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 100 nanoseconds) in immersion mode nucleation (see Fig. 1.), which is regarded as the most important nucleation mode for ice formation in clouds in the atmosphere. 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.

ACKNOWLEDGEMENTS

This work was supported by the Academy of Finland (CoE program grant no. 272041), by the Nordic Centre of Excellence CRAICC and by supercomputing resources at CSC - IT Center for Science.

REFERENCES

Effects of Coatings of Sulphuric Acid and Limonene SOA on the Mass-Mobility Relationship of Soot Particles


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Keywords: Soot-SOA interaction, effective density, dynamic shape factor

INTRODUCTION

Particles containing soot are commonly considered to have a warming effect on the climate, because they can strongly absorb solar radiations. However, secondary organic aerosols (SOA), formed by atmospheric oxidation of precursor gases, which are known to be a major fraction of atmospheric aerosols, can scatter light and act as cloud condensation nuclei (CCN), thereby having a cooling effect on the climate (IPCC, 2013). Soot, organic aerosols and sulphuric acid are likely to coexist, in diverse mixing states, and participate in complex interactions. Coatings such as sulphuric acid and SOA can modify the morphology of soot particles and change the optical properties and cloud forming properties significantly (Mikhailov et al., 2006).

METHODS

Differential Mobility Analyzer-Aerosol Particle Mass (DMA-APM) and the Tandem DMA techniques were used to study the effects of coating by sulphuric acid and Secondary Organic Aerosol (SOA) produced from limonene ozone oxidation on soot particle morphology. Amounts of sulphuric acid and limonene SOA coatings were changed step-wise and particle mobility diameter and mass were investigated. Derived properties, such as effective density, mass fractal dimension and dynamic shape factor were acquired from the measured mobility diameter and mass. Soot Particle - Aerosol Mass Spectrometer (SP-AMS) was used to study the chemical compositions of both fresh and processed soot particles.

CONCLUSIONS

Effective density of soot particles increased when more coatings were added to the surface. Generally, effective density decreased non-linearly when particle size of fresh soot increased. Soot particles coated with sulphuric acid and SOA also showed similar decreasing trend of effective density. Fresh soot particles become more compact probably due to surface tension forces when sulphuric acid and SOA condensed their surface.

Figure 1. Effective densities of fresh and processed soot particles at different coating conditions

Figure 2. Dynamic shape factor of fresh and processed soot particles, initial mobility diameter of the fresh soot was 100 nm.

Chemical compositions of fresh and coated soot particles measured with SP-AMS reveal that the processed soot particles were dominated by SOA.

ACKNOWLEDGEMENTS

This work was supported by the Swedish Research Council Formas and Modelling the Regional and Global Earth system (MERGE).

REFERENCES


VOCs and ordinary dust responsible for impaired air quality in indoor football arenas with artificial turf fields

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Keywords: indoor air, artificial turf, organic compounds

INTRODUCTION

Artificial turf fields, cushioned with rubber granulates for playing football, may cause inhalation exposure to dust or chemical agents (Dye 2006, Simcox 2011). Styrene butadiene rubber (SBR) granulates made from recycled vehicle tires contain potentially hazardous chemicals (PAH, VOC). They are commonly used also among about one hundred indoor football arenas in Finland.

METHODS

Four permanent arenas and two pressurized canvas domes were studied during usual daily activity in the end of winter season. VOC samples and particulate samples for PAH and metal analyses were collected along with continuous monitoring of fine (PM<2.5), thoracic (PM<10), and coarse particles.

VOC emissions and PAH contents were analyzed from rubber granulates vacuum-sampled from the field surface.

Health symptoms and nuisance experienced by football players were investigated using a structured questionnaire.

RESULTS AND CONCLUSIONS

The PM10 concentrations (10-20 µg/m³) in arenas were comparable to urban outdoor levels, but there was an indication of an indoor source of coarse (appr. 10-15 µm in diameter) dust (Table 1).

Table 1. Mean (SD) concentrations (µg/m³) of PM10 and coarse particles in and outside football arenas.

<table>
<thead>
<tr>
<th>Arena</th>
<th>PM10 (µg/m³)</th>
<th>Coarse PM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Indoor</td>
<td>Outdoor</td>
</tr>
<tr>
<td>1</td>
<td>8.2 (1.8)</td>
<td>10.9 (6.6)</td>
</tr>
<tr>
<td>2</td>
<td>17.2 (2.9)</td>
<td>18.2 (37)</td>
</tr>
<tr>
<td>3</td>
<td>22.1 (3.4)</td>
<td>10.1 (3.8)</td>
</tr>
<tr>
<td>4</td>
<td>16.0 (5.8)</td>
<td>19.6 (25)</td>
</tr>
<tr>
<td>5</td>
<td>21.1 (5.1)</td>
<td>11.0 (8.5)</td>
</tr>
<tr>
<td>6</td>
<td>13.2 (3.9)</td>
<td>32.3 (30)</td>
</tr>
</tbody>
</table>

The total PAH contents of three SBR granulate samples were much higher (38-65 mg/kg) than those of two other types of rubber granulates (0.1 and 2 mg/kg). The indoor air PAH concentrations were low in both gas and particulate phases in all arenas.

Total indoor air VOCs were high in one arena (440 µg/m³) with no proper ventilation. Some compounds (benzothiazole, aldehydes) were frequently found in both the granulate emission and indoor air (Figure 1).

Figure 1. Indoor air VOC concentration (µg/m³) in football arenas 1-6.

As many as 49 adolescent football players out of 90 (54%) reported at least one symptom or nuisance (dusty air, sore throat, running nose, odd smell, eye or skin irritation) during or after training in winter season. The indoor air of all the studied arenas was reported to cause some nuisance.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education and Culture and the Ministry of Social Affairs and Health.

REFERENCES


100
Highly reproducible method to determinate particle mass and density

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Keywords: filter collection, particle density, particle mass, Faraday cup

INTRODUCTION

Commonly, determination of particle density requires collecting particles on a filter where particle mass can be weighed. The number of the collected particles can be determined, e.g., by monitoring the number concentration before and after the filter. In this study, we conducted a simple experiment to determine the particle density. Our method enables determination of the number of collected particles by measuring the electric current directly from the filter.

METHODS

The main principle of the method is presented in Figure 1. The total volume of the collected particles is determined from the number size distribution measured with SMPS. Multiplying the distribution with particle volume and integrating over the whole size scale gives the particle volume concentration, \( C_v \), of the aerosol.

\[
N_{tot} = \frac{I}{Q \eta \epsilon \gamma}, \quad (1)
\]

where \( Q \) is volume flow through the FCUP, \( t \) sampling time, \( n \) number of elementary charges per particle, \( \epsilon \) elementary charge, \( \eta \) filtration efficiency of the FCUP and \( \gamma \) calibration coefficient of the electrometer. The filter is weighed before and after the collection. The difference of the two weighings is equal to the mass of the collected particles.

The total volume of the collected particles is determined according to Equation 2

\[
V_{tot} = C_v Q t. \quad (2)
\]

Finally, the density of the particles is

\[
\rho = \frac{m}{V_{tot}}. \quad (3)
\]

We determined the density of di-octyl sebacate (DOS, liquid at NTP) and stearic acid (SA, solid at NTP) particles. Four filter collections were sampled of both particle material resulting to four density values.

CONCLUSIONS

The determined densities and total number of the collected particles for each measurement (1-4) are shown in Table 1.

Table 1. Determined densities and number of collected particles. (Lide, 2008)

<table>
<thead>
<tr>
<th>Filter number</th>
<th>( \rho ) (kg/m(^3))</th>
<th>( N_{tot} ) (1/cm(^3))</th>
<th>( \rho ) (kg/m(^3))</th>
<th>( N_{tot} ) (1/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>903</td>
<td>1.1 \cdot 10^{10}</td>
<td>968</td>
<td>7.8 \cdot 10^{9}</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>1.2 \cdot 10^{10}</td>
<td>959</td>
<td>9.2 \cdot 10^{9}</td>
</tr>
<tr>
<td>3</td>
<td>889</td>
<td>9.6 \cdot 10^{9}</td>
<td>952</td>
<td>6.7 \cdot 10^{10}</td>
</tr>
<tr>
<td>4</td>
<td>845</td>
<td>1.1 \cdot 10^{10}</td>
<td>930</td>
<td>6.2 \cdot 10^{10}</td>
</tr>
<tr>
<td>Stdev</td>
<td>26.8</td>
<td>16.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>884</td>
<td>952</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \rho_{bulk} )</td>
<td>912</td>
<td>940</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The determined densities are in good agreement with literature bulk values. The reproducibility of the technique is extremely high which can be seen from the low deviation of the results. Somewhat bigger standard deviation of the determined densities of DOS might be due to possible evaporation of the liquid during long sampling time. The technique enables linking particle mass to electric current measurement; thus, enabling online-monitoring of particle mass.

ACKNOWLEDGEMENTS

This work was made in the Measurement, Monitoring, and Environmental Assessment (MMEA) research program (WP 4.5.1) of Cleen Ltd.

REFERENCES


Estimate of the radiative effect of brown carbon using AERONET products

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Keywords: Brown carbon, aerosol composition, aerosol direct radiative effect, AERONET

INTRODUCTION

Brown carbon (BrC) is considered a type of aerosol component, that is organic and whose light absorption is enhanced towards the shorter end of the visible radiation. It is often emitted into the atmosphere along with other organic aerosol mass, during biomass burning for instance, however its chemical composition is not strictly defined. The current understanding in the brown carbon loading in the atmosphere and its effects on the climate require improvement.

The strong spectral enhancement of light absorption by brown carbon is distinct to that of black carbon (BC), which provides an opportunity to quantify BrC concentration in atmospheric aerosols when aerosol absorption is characterized by measurements. In particular, AERONET remote sensing products on the spectral absorption of aerosols have the potential for separating certain aerosol components following this principle, see Schuster et al. (2005).

This work is an effort to estimate BrC concentrations by its spectral light absorption features and, further, to estimate direct radiative effect (ADRE) of BrC based on AERONET inversion products.

METHODS

The inference of aerosol composition was done by first assuming predefined imaginary refractive indices $k_i$ for absorbing aerosol components black carbon (BC), brown carbon (BrC), hematite and goethite, which are embedded within a scattering host. Then, the components were mixed to seek an optimal mixture, whose $k$ was corresponding to $k_{\text{AERO}}$ obtained from AERONET products.

This optimisation produced approximations for BrC concentrations for each AERONET observation. The concentrations were then used to calculate aerosol optical properties using the spheroid aerosol model by Dubovik et al. (2006), which allowed for a representation of aerosols consistent with AERONET. Finally, the radiative effect of BrC was calculated using libRadtran radiative transfer (Mayer and Kylling, 2005) simulations.

CONCLUSIONS

The spectral absorption properties of the four absorbing aerosol components were used for the quantification of the components. Preliminary results show an annual average of 3 \% BrC content in atmospheric aerosols at AERONET sites (ranging 0 \% to 7 \% by location). This, in addition to AERONET products, was utilized to estimate the optical properties and radiative effects of BrC. At AERONET measurement sites the annual average ADRE ranged between $\pm0.7\ \text{Wm}^{-2}$ and, thus, BrC appears to have both warming and cooling radiative effects due to its strong spectral enhancement of absorption and also due to other aerosol components present in the internal mixture.

This on going work aims to assess the climatic effects of carbonaceous aerosols globally by constraining a global climate model with atmospheric remote sensing observations.

ACKNOWLEDGEMENTS

This work was supported by Maj and Tor Nessling Foundation. We thank the AERONET team for their effort in establishing and maintaining the AERONET sites.

REFERENCES


INTRODUCTION

The ability of aerosol particles to act as cloud condensation nuclei (CCN) depends primarily on their size but also on their chemical composition. Anthropogenic emission sources, such as traffic, industry and energy production, produce both new particles with distinct chemical composition and vapours which change the size and composition of existing ones.

METHODS

In this study, the properties of cloud-activated particles are obtained during cloud events by measuring both cloud interstitial and total aerosols at Puijo measurement station (Leskinen et al., 2009). These measurements include particle number size distribution, aerosol light scattering and absorption, which were measured continuously since 2006. Other measurements include some climatically relevant gases (O\(_3\), NO\(_x\), SO\(_2\), CO\(_2\), CH\(_4\)). In addition, cloud droplet size distribution is measured during every autumn and spring.

A recent case study showed that the local sources, a paper mill and a heating plant, affect both the physical and chemical properties of the aerosol and thus, also clouds (Portin et al., 2014). To analyze the effects of the sources in more detail, a recent case study showed that the local emissions were measured continuously since 2006. Other measurements include some climatically relevant gases (O\(_3\), NO\(_x\), SO\(_2\), CO\(_2\), CH\(_4\)). In addition, cloud droplet size distribution is measured during every autumn and spring.

A recent case study showed that the local sources, a paper mill and a heating plant, affect both the physical and chemical properties of the aerosol and thus, also clouds (Portin et al., 2014). To analyze the effects of the sources in more detail, a recent case study showed that the local emissions were measured continuously since 2006. Other measurements include some climatically relevant gases (O\(_3\), NO\(_x\), SO\(_2\), CO\(_2\), CH\(_4\)). In addition, cloud droplet size distribution is measured during every autumn and spring.

RESULTS

Figure 1a shows the average total particle size distributions in cloud-free conditions for the different wind direction sectors. Figure 1b shows the mean size distribution of particles which have formed droplets. Both the total and activated particle size distributions are clearly dependent on the source. Heating plant, which has a lot of accumulation mode particles (D\(_p\) >100 nm), also produces more activated particles. The polluted sectors also have a higher concentration of smaller particles which are often present as quickly-varying bursts. This causes inaccuracies in the activation calculations, wrongly suggesting elevated concentrations of activated small particles, as shown in figure 1b.

The variation in the size of the activating particles is partly explained by the different shapes of the size distributions but the possibility that the particle chemical composition plays a role cannot be ruled out. Distinct pollutant plumes reached the station during 14 % of all cloud events, with variable concentrations of gases and black carbon depending on the source, suggesting that the particle composition is different as well. A careful analysis of each individual plume will be performed to obtain more detailed information on this matter.

REFERENCES


Variation of surface properties for atmospheric surfactant solutions with environmental parameters observed directly using synchrotron XPS

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Keywords: Aqueous aerosols, surfactants, acidity, synchrotron XPS.

INTRODUCTION

Surface active compounds (surfactants) are ubiquitous in atmospheric organic aerosols. Commonly found atmospheric surfactants are the long-chain carboxylic (fatty) acids and salts of their carboxylate anions. Studies of their cloud droplet activation thermodynamics have revealed that the influence of surfactant properties on organic aerosol cloud condensation nucleus (CCN) activity is governed by significant bulk-to-surface partitioning (Prisle et al., 2010). In general, due to the very large surface areas of sub-micron atmospheric aerosol particles, surface compositions and properties can be expected to pose a disproportionally large influence on aerosol processes and their impacts in the atmosphere (Prisle et al., 2012).

METHODS

We make direct observations of the surface chemical environment in aqueous solutions comprising different atmospheric organic surfactants (sodium formate, sodium acetate, sodium propionate, sodium butyrate, sodium hexanoate, and sodium octanoate), using synchrotron-based X-ray Photo-electron Spectroscopy (XPS) on a liquid micro-jet. All experiments were performed at the Swedish national synchrotron facility MAX IV Laboratory, Lund University, at the soft X-ray beamline I411. XPS is a highly chemically sensitive and surface specific spectroscopic technique and therefore ideal for studying the adsorption of surfactants in the aqueous surface region (Bergersen et al., 2007). We have obtained unique insights into how the composition of the surface differs from that of the bulk, in terms of organic enrichment and chemical speciation, and how these quantities are affected by important environmental parameters such as aqueous concentration, added salts, and pH of the aqueous phase.

CONCLUSIONS

Consistent with our recent work, we observe that in aqueous mixtures with inorganic salts containing ammonium cations, surface active carboxylate anions are protonated in the surface region to yield the corresponding carboxylic acids, to an extent which is much greater than expected from the respective bulk solution concentrations and Brønsted acid and base strengths involved. This strongly enhanced protonation occurs specifically in the aqueous surface region and significantly changes the surface composition with respect to the bulk solute, without any accompanying similar change in aqueous bulk phase properties, in particular the solution pH. (Prisle et al., 2012). With increasing ionic strength, salting out in general pushes more of the carboxylate anions to the aqueous surface region, but only in ammonium solutions does increasing the amount of ions significantly affect the abundance of acid in the surface. By measuring surface titration curves for aqueous surfactant solutions using XPS, we have derived “effective acid constants” for surface adsorbed surfactants analogous to the traditional Henderson–Hasselbalch equation, which indicate a significantly more acidic environment in the surface, compared to the associated bulk. Future work will be directed at gaining more insight into the quantification and underlying mechanisms of such aqueous surface-specific acidity.

ACKNOWLEDGEMENTS

This work was supported by the NordForsk researcher network project 10160 NICITA, the Knut and Alice Wallenberg Foundation (KAW), the Swedish Research Council (VR), and the Finnish Centre of Excellence in Atmospheric Science: From Molecular and Biological processes to the Global Climate (grant no. 272041). N. L. Prisle gratefully acknowledges personal funding from the Carlsberg Foundation (grants 2009_01_0366 and 2010_01_0391) and the Finnish Academy of Sciences (257411).

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The effect of fine filter type in ventilation unit on I/O-ratios of PNC, PM$_{2.5}$ and PM$_{10}$ in a 21st century apartment – a pilot study

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Keywords: outdoor air, indoor air, particulate matter, infiltration

INTRODUCTION

Fine particles (PM$_{2.5}$) originating from ambient outdoor air cause annually 6000 lost healthy life years per million inhabitants in Europe (Hänninen et al. 2014). A major part of exposure, in Finland approximately 57%, occurs at home indoors (Schweizer et al. 2007). By improving the filtration efficiency of supply air above the current standard filter F7 for fine PM, it may be possible to significantly reduce personal exposures of urban and suburban residents to outdoor air pollutants.

The aim of this pilot study was to monitor the effect on indoor air quality of an electrically charged synthetic F9 vs. ordinary cellulose F7 fine PM filter placed in a semiautomatic mechanical ventilation unit of a 5-year-old apartment.

METHODS

A pilot study was conducted in one 120 m$^2$ apartment in two floors of a row house built in 2009 in suburban Kuopio, Finland. The measurement period was four days in early spring 2014.

Particle number concentration (PNC – size 0.02-1 μm), and the concentrations of PM$_{2.5}$ and thoracic particles (PM$_{10}$) were measured simultaneously from ambient indoor and outdoor air using optical analysers (Ptrak 8525, DustTrak DR5533). Different filter setups (duration) in the ventilation unit were: 1) new G4 coarse + new F9 fine filters (7.25 h), 2) three months old G4 coarse +F9 fine filter s (33.5 h), and 3) three months old coarse G4 and clean F7 fine filters (10 h).

The occupants kept activity diary and they were instructed to avoid residential activities (cooking, window opening etc.) known to produce peaks in indoor PM levels.

RESULTS AND CONCLUSIONS

The use of especially new F9 (setup 1) but also three months old F9 fine filter (setup 2) in ventilation unit seems to decrease the I/O-ratios of PM$_{2.5}$ and PM$_{10}$ when compared to the use of clean F7 filter (setup 3). A similar difference was seen only with new F9 in PNC that was more sensitive to a variety of indoor emissions than the PM mass measurements (Table 1).

<table>
<thead>
<tr>
<th></th>
<th>PNC #/cm$^3$</th>
<th>PM$_{2.5}$ μg/m$^3$</th>
<th>PM$_{10}$ μg/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>in</td>
<td>570 (250)</td>
<td>4.1 (1.4)</td>
</tr>
<tr>
<td></td>
<td>out</td>
<td>3300 (1300)</td>
<td>29 (1.8)</td>
</tr>
<tr>
<td>I/O-ratio</td>
<td>0.20</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>2</td>
<td>in</td>
<td>760 (460)</td>
<td>6.6 (1.3)</td>
</tr>
<tr>
<td></td>
<td>out</td>
<td>3200 (2040)</td>
<td>34 (10)</td>
</tr>
<tr>
<td>I/O-ratio</td>
<td>0.30</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>in</td>
<td>600 (70)</td>
<td>5.6 (0.6)</td>
</tr>
<tr>
<td></td>
<td>out</td>
<td>2300 (500)</td>
<td>21 (1.3)</td>
</tr>
<tr>
<td>I/O-ratio</td>
<td>0.29</td>
<td>0.27</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The results of this pilot study should be treated with caution because some measurement periods were too short to reach an equilibrium state indoors after filter exchange. The time-lags between temporal variations in outdoor and indoor PM concentrations have not been taken into account when calculating the I/O-ratios, but there were only few larger short-lasting variations during the study period. The pilot study gives a good basis for future experiments with longer filter setup periods in residences locating in vicinity to busy traffic and prevalent wood burning.

REFERENCES

NOx dependency of HOM formation in chamber studies

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Keywords: HOM, particle formation, BVOC oxidation

INTRODUCTION

Biogenic volatile organic compounds (BVOC) have been considered an important factor in new particle formation and particle growth, but the formation pathway from BVOC to particle phase was long unknown. Recently, it has been suggested that a newfound class of compounds, highly oxidized multifunctional molecules (HOM), could be the compounds linking gas phase and particle phase (Ehn et al., 2012, 2014, Schobesberger 2013).

Peroxy radical combined with an internal H-shift has been suggested as a formation pathway from BVOC to HOM (Rissanen et al., 2014, Mentel 2014, submitted). Here we present data of the NOx dependency of HOM formation from α-pinene via OH oxidation under different NOx concentrations. Our findings from NOx experiments further confirm that peroxy radicals play a key role in HOM formation. Formed HOM nitrates behave as expected from classical peroxy radical chemistry.

METHODS

According to classical chemistry, peroxy radicals have few possible reaction pathways:

\[
\text{RO}_2^* + \text{R}'\text{O}_2^* \rightarrow >\text{CHOH} \quad (\text{Alcohol})
\]
\[
\rightarrow >\text{C}=\text{O} \quad (\text{Ketone})
\]
\[
\rightarrow >\text{CHOOH} \quad (\text{Hydroperoxy})
\]
\[
\rightarrow >\text{CHO}^* \quad (\text{Alkoxy radical})
\]
\[
\rightarrow \text{ROOR}' \quad (\text{Dimer})
\]

When adding NO to the system, another pathway becomes increasingly dominant in the expense of other pathways, forming organic nitrates:

\[
\text{RO}_2^* + \text{NO} \rightarrow \text{RO}^* + \text{NO}_2
\]
\[
\rightarrow \text{RONO}_2
\]

Adding NOx into the system first increases the total HOM formation (Figure 1). Further increase of NOx decreases the HOM production. Increased NOx concentration has been observed to inhibit new particle formation but not particle mass formation (Wildt et al., 2014). Figure 1 also shows dimer concentrations decreasing faster with increased NOx compared to monomer concentrations, which would suggest that dimers are the main HOM to participate in new particle formation.

CONCLUSIONS

Increasing NOx condition shifts the formation pathways of HOM towards organic nitrates (Figure 2). This competes with dimer formation pathway, leading to less dimer formation, which causes less particle formation under higher NOx conditions. The total HOM formation is also inhibited.

ACKNOWLEDGEMENTS

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Black carbon mixing state in India

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INTRODUCTION

Absorbing aerosols are warming the global climate; however, uncertainties are still significant partly due to the lack of detailed aerosol measurements. Especially black carbon mixing state is poorly characterized (Bond et al., 2013). Due the significant local and regional emissions, Northern India is one of the global absorbing aerosol hotspots. It has been suspected that absorbing aerosols could have an effect on the monsoon, which has great importance for the region.

Aerosol optical properties and cloud forming potential depend on the black carbon mixing state. Although total concentration is measured routinely, few instruments provide information about the mixing state. One of such instruments is Single Particle Soot Photometer or SP2 (Stephens et al., 2003), which detects refractory black carbon (rBC). SP2 can measure the fraction of rBC-containing particles and the mass of rBC in each particle. We have further developed the method by coupling a differential mobility particle sizer (DMPS) with a SP2; this system provides even more accurate and size-resolved information about rBC mixing state.

METHODS

Mixing state of rBC aerosol was measured by the DMPS-SP2 system in Northern India in Mukteshwar and Gual Pahari during winter and spring 2014, respectively. Mukteshwar is a relative clean site at the foothills of the central Himalayas about 2 km above the Indo-Gangetic plains (IGP) and Gual Pahari station close to Delhi where aerosol concentrations are significantly higher (e.g. Raatikainen et al., 2014). Total rBC mass concentrations, rBC size distributions and the mixing state parameters were measured as a function of particle size and time. Figure 1 shows diurnal cycle of the total rBC mass concentrations, particle to rBC core diameter ratios and the fractions of rBC containing particles. The latter two parameters are calculated for 360 nm size class. The particle to core diameter ratio is based on an assumption that spherical rBC cores are coated by a non-absorbing material such as sulphate.

![Figure 1. Diurnal cycles of rBC mass concentrations, particle to rBC core diameter ratios and fractions of particles containing rBC.](image)

CONCLUSIONS

Total rBC concentrations are significantly higher at the IGP site Gual Pahari than those at the central Himalayan foothill site Mukteshwar. Large fractions of particles contain rBC in Gual Pahari, but the fraction is decreased when air masses are transported from the plains to the Himalayan foothills. Practically all rBC particles are internally mixed and thickly coated.

ACKNOWLEDGEMENTS

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Connecting the solubility and CCN activation of complex organic aerosols: A theoretical study using the Solubility Basis Set (SBS)

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INTRODUCTION

Organic aerosol particles often consist of thousands of compounds with different properties. One of these properties is solubility, which affects the hygroscopic growth and CCN activation of the organic particles. Here we investigate the CCN activation behavior of complex organic aerosols accounting for the distribution of solubilities present in these mixtures.

METHODS

We considered a monodisperse population of spherical aerosol particles consisting of an internal mixture of organic compounds. When exposed to water vapor, these particles were assumed to grow reaching a thermodynamic equilibrium between the water vapor and the particle phase. The composition of the organic and aqueous phases was determined on one hand by the equilibrium between the aqueous phase and water vapor, and on the other hand by the equilibrium of the aqueous phase with the organic insoluble phase. We modelled the mixtures with the help of a solubility basis set (SBS, analogous to the volatility basis set VBS, Donahue et al. 2006, 2011, 2012), describing the mixture with $n$ surrogate compounds with varying solubilities. We varied the range and shape of the solubility distribution, and the number of components $n$ in the distribution, we also assumed two different kinds of interactions between the organic compounds in the insoluble phase 1) ideal mixture, where organics limit each other’s dissolution; 2) unity activity, where organics behave as pure compounds and do not influence each other’s dissolution. Critical supersaturations and the dissolution behavior at the point of CCN activation were calculated utilizing the Köhler theory for all organic mixtures (denoted here as the “full model”).

The full model predictions were compared with the three simplified models: 1) assuming complete dissolution of all compounds; 2) treating the organic mixture solubility with the hygroscopicity parameter $\kappa$ and 3) assuming a fixed soluble fraction $\epsilon$ for each mixture.

RESULTS AND CONCLUSIONS

The comparison between the full model and the complete dissolution assumption demonstrated a systematic under-prediction (up to 40%) of the activation diameter, while the $\kappa$ and $\epsilon$-based solubility models were generally within 10% (in most cases within 5%) of the activation diameter predicted using the full solubility distribution representation, see Fig 1. The $\epsilon$ and $\kappa$ values were found to correspond to the fraction of material with solubilities larger than a given threshold solubility $c_t$. The median threshold assuming the organics to form an ideal mixture was 10 g L\textsuperscript{-1}, with most of the $c_t$ values falling between 1 and 100 g L\textsuperscript{-1}. For the unity organic activity assumption this median threshold was 1 g L\textsuperscript{-1}, with most of the $c_t$ values falling between 0.1 and 10 g L\textsuperscript{-1}. Our results suggest that the solubility range causing limited dissolution in CCN activation is between 0.1-100 g L\textsuperscript{-1} but in most cases material below 1 g L\textsuperscript{-1} is practically insoluble and material above 10 g L\textsuperscript{-1} completely soluble upon CCN activation at atmospheric supersaturations.

Figure 1. The performance of the simplified models in predicting the activation diameter as compared with the full model. The black bars depict the 25 and 75 percentiles and the gray bars the 10 and 90 percentiles.

REFERENCES

Formation of highly oxidized multifunctional compounds by autoxidation of cyclohexenes

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Keywords: autoxidation, aerosol precursors, highly oxidized molecules, ELVOC

INTRODUCTION

Recently, the formation of highly oxidized molecules by gas-phase processing of volatile organic compounds (VOC) has received considerable attention, mainly due to its potential importance in secondary organic aerosol (SOA) production in the ambient atmosphere. The highly-oxidized product species are believed to be formed by sequential peroxy-radical rearrangement and oxygen addition reactions, so-called autoxidation (Crounse et al. 2013, 2013), leading to high oxygen contents by pseudo-unimolecular reaction steps.

In our previous work we illustrated the generality of this process in producing highly oxidized material from biogenic sources (Ehn et al. 2014, Jokinen et al. 2014), as well as described the details of the oxidation progression in a more simplified surrogate system of cyclohexene (Rissanen et al. 2014). The current work describes the continuation of this work in trying to understand how the different structures of the precursor compounds translate into specific structures in the obtained mass spectra. Thus the previous cyclohexene investigation was extended to include 1- and 4-methylcyclohexene oxidation systems, as well as a few other unsaturated species with endo- and exocyclic double bonds.

METHODS

The alkene oxidation experiments were performed in various glass flow tubes under ambient laboratory conditions using N₂ or synthetic air as a bath gas. The oxidation reactions were initiated by ozonolysis and the highly-oxidized products were detected using a Chemical Ionization Atmospheric Pressure interface Time-of-Flight (CI-API-TOF) mass spectrometer with nitrate ion (NO₃⁻) based charging of the sample molecules. The volumetric flow rate was 10 lpm which resulted in about 2 to 20 s residence times in the flow tubes employed. Supplemental information was gathered from investigations where water or deuterated water was added to the reaction mixture. In addition, the likelihood of a few proposed oxidation pathways was further assessed by quantum chemical calculations, using our previously validated approach from the cyclohexene system (Rissanen et al. 2014).

CONCLUSIONS

Large amount of previously unidentified, highly-oxidized product species, with O/C as high as 1.5 in the monomers were detected, with the structure of the olefinic precursor heavily influencing the observed product distributions. While the methycyclohexenes investigated in the current work seem to oxidize according to guidelines found previously for cyclohexene autoxidation, the more complicated structures of the biogenic alkenes result in significantly more complicated mass spectra, and thus also lead to more ambiguity in the proposed final product structures.

ACKNOWLEDGEMENTS

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REFERENCES

Contribution of ELVOC to the growth and phase state of SOA particles
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Keywords: ELVOC, SOA formation, gas-phase chemistry, particle-phase mass transfer limitations

INTRODUCTION
Recent field and laboratory experiments have identified large- and rapid formation of extremely low-volatile organic compounds (ELVOC) (Ehn et al., 2014).

METHOD
We have evaluated and constrained the proposed ELVOC formation mechanism from Ehn et al. (2014) using the Aerosol Dynamics, gas- and particle-phase chemistry kinetic multilayer model for laboratory CHAMber studies (ADCHAM) (Roldin et al., 2014). The improved ELVOC mechanism is now implemented into the process-based chemistry transport models ADCHEM (Roldin et al., 2011) and SOSAA (Boy et al., 2011). In all models the ELVOC mechanism is fully coupled to the master chemical mechanism (MCMv3.2) gas-phase chemistry (Saunders et al., 2003). Together with ADCHAM we use different datasets to evaluate: (i) the ELVOC formation mechanism (Ehn et al., 2014), (ii) the contribution of ELVOC to the growth of homogeneously nucleated particles (Ehn et al., 2014) and (iii) how ELVOC influence the phase-state and the mass-transfer limited evaporation of SOA particles (Vaden et al., 2011).

INTRODUCTION
With an updated ELVOC formation mechanism (including unimolecular ELVOC peroxy radical termination (Rissanen et al., 2014)) ADCHAM captures the main features of the ELVOC SOA mass formation (Fig. 1) and the ELVOC(g) mass spectrum (Fig. 2) measured during the Jülich Plant Atmosphere Chamber (JPAC) experiments by Ehn et al., 2014.

Figure 1. Modelled [ELVOC(g)] and SOA mass during an ammonium sulphate (AS) seed particle experiment in JPAC (Ehn et al., 2014). Given are both the total SOA and the SOA formed exclusively from MCM (SVOC and LVOC) oxidation products.

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Figure 2. Modelled mass spectrum from an experiment with 6.4 ppb α-pinene, 0.1 ppb NO, 1 ppb NO\(_2\) and 78 ppb O\(_3\).
Modeling aerosol growth by extremely low-volatility organic compounds

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Keywords: Aerosol modeling, Organic aerosols, Aerosol dynamics

INTRODUCTION

We used the model MALTE-BOX to model the condensational growth of aerosol. The model simulated a period of 11 days in May 2013 at the SMEAR II station in Hyytiälä. The air chemistry included the standard Master Chemical Mechanism chemistry and was extended with ELVOC (Ehn et al. (2014)) molecules.

METHODS

MALTE-BOX is an improved zero-dimensional version of the Model to predict new Aerosol formation in the Lower Troposphere described by Boy et al. (2006). It combines several models to simulate air chemistry, emissions and aerosol dynamics. In this study only air chemistry and condensation were studied.

Equations for chemistry were acquired from MCM, Master Chemical Mechanism v3.2 (Jenkin et al., 1997; Saunders et al., 2003), and calculated with KPP, the Kinetic PreProcessor (Damian et al., 2002).

Aerosol dynamics were simulated with University of Helsinki Multicomponent Aerosol model, UHMA, described in Korhonen et al. (2004). The aerosol distribution for each day was initialized from DMPS measurements.

Modeling condensation requires several vapor properties to be known and we used estimation methods to calculate them from the molecular structure of the vapors. We used the method described in Nannoolal et al. (2008) to estimate the saturation vapor pressures of the vapors and the method described in Fuller et al. (1966) to estimate their diffusion volumes. We used the method from Girolami (1994) to estimate the liquid densities of the compounds.

CONCLUSIONS

The ELVOC molecules increased the condensation of organic molecules in the simulations. On average the increase was an order of magnitude. We are currently investigating how much changing the molecule structures or chemical mechanism affects the condensation.

ACKNOWLEDGEMENTS

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First results from continuous measurements of particle size distribution and black carbon concentration in Nanjing

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Keywords: air pollution, black carbon, aerosols

INTRODUCTION

China has encountered air quality problems in recent years due to rapid industrialization. Measurements of particle mass and gas species are conducted in many Chinese cities but climatically more relevant particle size distribution and black carbon measurements are still quite rare.

Our measurements were conducted in Nanjing in co-operation with Nanjing University (NJU). Nanjing is a Chinese megalopolis in the Yangtze River Delta (YRD) region with approx. 8 million inhabitants. The main regional air pollution sources are industry, traffic, energy production with coal and burning of agricultural wastes (Ding et al. 2013). In Nanjing, the main industries are electronics, automotive, smelters and petrochemistry (Hu et al. 2013). The YRD region is one of the most densely populated areas in China and the region suffers from severe air pollution (Ding et al. 2013).

Continuous size-segregated measurements of particle number size distribution and black carbon concentration with good time resolution will provide more insight knowledge of the regional sources and their emissions both in air quality and climate perspective.

METHODS

The measurement station is located at NJU Xianlin campus on a rooftop of a five-floor building. The measurements include: NanoScan SMPS Nanoparticle Sizer with number size distribution from 10 nm to 420 nm, Optical Particle Sizer Spectrometer with number size distribution from 0.3 μm to 10 μm, Magee Scientific Aethalometer AE-42 with 7 wavelengths (light absorption by particles, black carbon & brown carbon) and Vaisala WX-520 weather station. The time resolution for the size distribution measurements is 1 min and for the absorption/black carbon 2 min. The weather station has been measuring since May 2013 while the particle instruments were installed in early November 2014. At the same station hosted by NJU, continuous measurements of different PM fractions (PM10, PM2.5 & PM1) are carried out along with numerous gas species (SO2, H2S, NO, NO2, NH3, O3 & CH4+UV-DOAS measurements).

CONCLUSIONS

The continuous aerosol measurements are combined with the local air quality and weather data to obtain more detailed size-segregated properties of the local aerosol and their sources. 120-hour backward trajectories will be calculated in three-hour interval with HYSPLIT model. The trajectories will be used to define the origin of the air masses from sources further away from our site and local wind data is used for defining the nearby sources. All this will be combined with the local emission inventories currently under preparation at NJU. The good size and time resolution of the new instruments will enable a better source identification for the emissions.

The measurements will continue at least for one year, collecting valuable information about particle size distributions, black and brown carbon concentrations and weather variables. One-year dataset provides an opportunity to investigate the seasonal variations of the emissions from different sources. The possible diurnal emission patterns will also be revealed.

ACKNOWLEDGEMENTS

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REFERENCES

Gas phase synthesis of iron nanoparticles with simultaneous reaction and dilution

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Keywords: chemical vapour synthesis, iron oxide, dilution, APCVS

INTRODUCTION

Chemical vapour synthesis (CVS) is a widely used method for nanoparticle (NP) production (Swihart, 2003). Recently atmospheric pressure CVS method with controlled oxidation was used to synthesize nanosized iron oxides by Ruusunen et al. (2014). However, the wall losses and good control over the primary size of the NPs can be a problem when the APCVS method is used.

METHODS

In this study we present an improved method for nanoparticle production based on APCVS method and continuous dilution with reaction gas (O2/N2). The reactor consisted of a precursor feed system, a feeding probe, a porous tube reactor and a porous tube diluter. Iron and iron oxide NPs were synthesized by using iron pentacarbonyl as the precursor. The precursor feed was produced by bubbling a carrier gas (N2, 0.5 lpm, 20°C) through a reservoir of the liquid precursor. The precursor vapour was, then, carried through the feeding probe into the porous tube reactor. The reaction gas consisted of nitrogen and a controlled amount of oxygen (0 or 0.3 v-%) and was fed with a flow rate of 5 lpm uniformly through the porous tube reactor where it was mixed with the precursor vapour at the temperature of the reactor set to 600°C. Finally, the exiting aerosol was diluted with a large amount of N2 (60 lpm, 20°C).

The particle number size distributions were measured directly from the gas phase with a SMPS. In addition, powder sample was collected for the TGA, the KD and the magnetic characterization with a planar filter. Moreover, a thermodynamic equilibrium and a computational fluid dynamics models were used to gain insight into the NP synthesis and the flow dynamics.

CONCLUSIONS

Geometric mean diameters (GMD), the geometric standard deviations (GSD) and number concentrations as measured by the SMPS are presented in Table 1. The GMD of the aggregates were relative large. However, the primary sizes of the NPs are in the nanoscale according the TEM images (Figure 1). The KD data shows that maghemite was obtained with oxygen concentration of 0.3 v-%, whereas pure iron was produced when no oxygen was available.

Table 1. GMD, GSD and number concentrations, for the NP aggregates as measured by SMPS.

<table>
<thead>
<tr>
<th>Amount of oxygen [%]</th>
<th>GMD [nm]</th>
<th>GSD</th>
<th>Number concentration [10^3 cm^-3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>150</td>
<td>1.8</td>
<td>4.6</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>2.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

In this paper we presented the APCVS method based on continuous dilution with reaction gas. It is shown that the wall losses can be prevented and the primary particle sizes of the synthesized NPs remain relative small due to the continuous dilution. The presented method offers an alternative way to produce NPs with the APCVS method.

ACKNOWLEDGEMENTS

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REFERENCES

Nucleophilic substitution reactions of partially hydrated superoxide anions with alkyl halides

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Keywords: superoxide, hydration, SN₂, methylhalide

INTRODUCTION

The superoxide anion, O₂⁻, is a primary anion in the atmosphere, typically formed by a three body electron attachment reaction. It has also been found that the superoxide ion is formed and used in the reactions of transition metals in atmospheric droplets (Graedel et al., 1986). We wish to better understand how the reactions of the superoxide anion is influenced by the degree of hydration; for this purpose we have studied the well-known nucleophilic substitution reaction type 2 (SN₂) where the superoxide, acting as a nucleophile and with 0–5 water molecules attached, reacts with methyl chloride or methyl bromide. The interpretation of the experimental results is aided by quantum chemical calculations. The reactions of the superoxide anion can also be of relevance for peroxyradicals.

METHODS

The experimental work was performed using a quadrupole-time-of-flight mass spectrometer. Calculations were performed using GAUSSIAN 09, using the hybrid density functional B3LYP, in conjunction with the 6-311G(d,p) basis set.

CONCLUSIONS

It was found that for the reactions between superoxide/water cluster anions and CH₃Cl, the corresponding reaction rates decrease in an exponential fashion when the number of water molecules increases. This can be seen in Fig. 1. A ligand exchange reaction was also observed, in which methyl chloride was incorporated into the cluster, followed by loss of a few water molecules. Similar results have been found for the reaction involving CH₃Br instead of CH₃Cl.

In nice agreement with these experimental findings, our Density Functional Theory calculations clearly indicate that the attachment of water molecules to superoxide anion is translated into much higher SN₂ activation barriers, i.e., from a practically barrierless process for the reaction between bare O₂⁻ and CH₃Cl to barrier heights in the range of 6–13 kJ mol⁻¹ for O₂⁻(H₂O) or even higher values for O₂⁻(H₂O)₂. These results confirm the role of O₂⁻ as a possible organic halide scavenger when solvated by only a few water molecules. This role is severely hampered by greater solvation. Although disproportionation of O₂⁻ is known to be a problem in water solution, it seems to not be an issue in small water clusters.

Figure 1. Relative rate coefficients for O₂⁻(H₂O)ₙ + CH₃Cl leading to Cl⁻ formation (nucleophilic substitution) and to CH₃Cl incorporation. The data is given for different centre-of-mass collision energies and cluster sizes n, and have been normalized to the Cl⁻ formation reaction of O₂⁻ at 0.8 eV. Error bars represent one SD due to count statistics.

REFERENCES

The analysis of metals by using Soot Particle Aerosol Mass Spectrometer

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Keywords: aerosol mass spectrometry, metals, black carbon

INTRODUCTION

Atmospheric aerosol contains trace metals that can be originated e.g. from various combustion processes, soil dust, sea-salt and industrial sources. Metals are frequently associated with adverse health effects and e.g. Cr, Mn and Ni are among hazardous air pollutants listed by EPA. Usually metals have been determined from particles by offline methods (e.g. X-ray Fluorescence from filter/impactor samples), however, due to their low concentrations in ambient air, long sampling times (typically 24-72h) have been necessary. That has prevented the investigation of short-term plumes or diurnal cycles of metals and has made the source apportionment analysis of metals demanding.

Online methods, like Soot Particle Aerosol Mass Spectrometer (SP-AMS) allows the detection of several metals in real-time, however, the mass quantification of metals is challenging and hasn’t been accomplished totally yet.

This study combines the results from the laboratory, emission and ambient air measurements in order to describe the determination of metals by using the SP-AMS. The aim of laboratory tests was to develop a method for the quantification of metals. Emission measurements showed the sources of metals and ambient measurements presented a set-up for the detection of low levels of metals in urban background site with a particle concentrator.

METHODS

Key instrument of this study was Soot Particle Aerosol Mass Spectrometer (Aerodyne Research Inc.) that is described in Onasch et al. (2012). Laboratory tests were performed in the Finnish Meteorological Institute (Carbone et al., 2014), emission measurements in an oil-fired heating station in Helsinki and in the vicinity of ore processing facility, and ambient measurements were conducted at SMEAR III site in Helsinki. In ambient measurement a particle concentrator (m-VACES; Saarikoski et al., 2014) was deployed.

CONCLUSIONS

In laboratory tests 13 different metals (Na, Al, Ca, V, Cr, Fe, Mn, Ni, Cu, Zn, Rh, Sr and Ba) were tested. Relative ionization efficiency (RIEmeas) was measured for each metal and theoretical relative ionization efficiency (RIEtheory) was estimated by using the value of the first ionization energy (φ) of the metal. The ratio of RIEtheory to RIEmeas was larger than one for Na, Rh, Ca, Sr, Ba, Al and V due to the thermal surface ionization and close to one for the transition metals (Mn, Fe, Zn, Cu and Cr). The RIEmeas values obtained by this method were applied to the data from the measurements in a heavy fuel oil fired heating station.

In a heating station Na, Mg, K, Ca, V, Cr, Fe, Ni, Cu, Zn, Rh, Sr, Sb, Cd and Ba were detected in the particle emissions. In ambient measurement in Helsinki eight metals (Al, V, Fe, Zn, Rb, Sr, Zr and Cd) were detected with the SP-AMS of which three (Sr, Zr and Cd) were observed only with the particle concentrator.

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Single Microbe Particle Characterization using Electro-Dynamic Balance

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Keywords: microbe, fungal spores, bacteria, LIBS

INTRODUCTION

Exposure to airborne microbes, such as bacteria and fungal spores, can cause adverse health effects for people. These particles are also interesting from the point of atmospheric processes because of their capability of acting as ice nuclei. This study is part of ongoing development of new methods for characterizing airborne microbes. We demonstrate a new combination of electro-dynamic balance (EDB) technique and laser spectroscopy. In the EDB, electrically charged single aerosol particles can be levitated in a certain point having small spatial fluctuation (Heinisch et al., 2009). Then, various properties of particles can be measured using laser based techniques, such as laser-induced breakdown spectroscopy (LIBS), Raman and laser-induced fluorescence (LIF) spectroscopy.

METHODS

An EDB chamber was designed and built using similar electrodes as reported by Heinisch et al. (2009). The idea is to generate an electrically charged single droplet from microbial suspension, and then trap and levitate the droplet in the EDB chamber until it is dried. The particle was illuminated by a 532 nm green laser. A low energy 355 nm laser pulse was used to excite autofluorescence from the particle. Fluorescence emission was measured with a spectrometer and an ICCD camera. After that a high energy 355 nm beam was used to break down the particle and to generate plasma. Emission spectrum from the plasma was measured with the spectrometer and the ICCD camera. The experimental setup is shown in Fig. 1. Good position stability of the particle in the EDB chamber enables using lower laser energy to generate the plasma, and very good detection limits for elemental components can be achieved. We report LIBS and LIF measurements of bacterial spores (Bacillus aureus) as well as fungal spores (Aspergillus versicolor and Penicillium brevicompactum) levitated in the EDB chamber. To our knowledge, this is the first study wherein the EDB technique was used to characterize microbe particles.

RESULTS AND CONCLUSIONS

Results showed that fluorescence spectra from the bacterial particles were different compared to the fungal particles. Ca, K and Na were typical compounds in the LIBS spectra from the microbes. This study demonstrates that LIBS and LIF spectra can be measured from single spores. By combining the LIBS with the LIF measurements, different types of microbes may be identified in real environment. The next step will be developing a real-time combined LIF and LIBS measurement system for analysis of ambient aerosol particles (e.g. mineral dust, fungal spores, bacteria, pollen).

ACKNOWLEDGEMENTS

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REFERENCES

Particulate associated polycyclic aromatic hydrocarbon emissions from different biodiesel fuel blends

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Keywords: biodiesel, PAH, exhaust emissions, Oxygenated PAHs

INTRODUCTION

Biodiesel is a renewable and biodegradable alternative to conventional diesel fuel that reduces the need for petroleum imports. Diesel exhaust particulates have recently been classified as carcinogenic to humans by IARC. However, the impact from biodiesel exhaust on human health is not fully known (Swanson et al., 2007).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants formed from incomplete combustion of organic material. The mutagenic and carcinogenic properties of PAHs are well known (Boström et al., 2002; IARC, 2010) and are suggested to play an important role on the adverse health effects from particulate inhalation (de Kok et al., 2006). Vehicular traffic and in particular diesel exhaust emissions is one of the major sources of particulate associated PAHs in the urban environment (Boström et al., 2002).

METHODS

In two separate studies; diesel particulate exhaust emissions were analysed from two different types of engines – one portable power generator (running at a constant load of near 100%) and one Volvo engine (Volvo TD40 GJE, 4.0 L, 4 cylinders). The TD40 engine was running under variable load, according to the urban part (10 min) of the European Transient Cycle, to mimic urban driving conditions. Particulate emissions from three different fuels; petroleum diesel, 30 wt% RME (B30) and 100% RME (B100) were sampled.

The particulates were sampled on Pallflex filters and extracted with pressurized fluid extraction. The extracts were analysed for more than 40 PAHs and 4 oxygenated PAHs (only the TD40 engine) using HPLC–GC/MS.

CONCLUSIONS

The sum of the mass fractions of the PAHs on the B100 particulates was lower than conventional diesel fuel in both of the studies. B30 and B100 particulates from the power generator had 36% and 74% lower content of PAHs than petroleum diesel respectively. Preliminary results of the PAH content of the particulates from the TD40 engine running on B30 did not differ from petroleum diesel while B100 particulates had 48% lower PAH mass fraction. For both engines, the particulates originating from petroleum diesel fuel combustion contained a higher fraction of methylated phenanthrenes than the particulate originating from B100 combustion; this is most likely a result of unburned petroleum diesel fuel that contains methylated PAHs. Furthermore, particulates originating from B100 combustion in the power generator contained a higher fraction of higher molecular weight PAHs than the other tested fuels. This effect was also the case for the TD40 engine, although less pronounced.

In contrast to the average mass fraction of particulate associated PAHs, the fraction of oxygenated PAHs (quinones) increased with increasing content of RME in the fuel.

A thermogravimetric analysis of the particulates from the power generator showed that the biodiesel particulates contained a substantial amount of volatile components, which was identified as fatty acid methyl esters using mass spectrometry. These results suggest that biodiesel exhaust particulates are chemically different from petroleum diesel particulate exhaust.

ACKNOWLEDGEMENTS

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REFERENCES


Effects on air quality of fossil vs. renewable diesel fuel switching in modern non-road vehicles in underground mine (HIME-project)

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Keywords: particulate matter, black carbon, nitrogen dioxide, PAH

INTRODUCTION

WHO International Agency for Research on Cancer (IARC) has classified diesel engine exhaust as carcinogenic to humans. A recent study involving over 12 000 workers from non-metal mines in the US highly influenced this decision. Long-term levels of respirable black carbon (BC) in emissions of diesel vehicle exhaust were associated with a greatly increased risk of lung cancer (Attfield et al. 2012).

Replacement of fossil diesel fuel with renewable, hydrogen-treated vegetable oil (HVO) has been shown to decrease all regulated and many unregulated emissions from EURO 4 heavy engines equipped with various after-treatment technologies (Murtonen et al. 2010). The aim of this study was to test the potential of HVO to reduce air concentrations of black carbon (BC), PAHs and particulate mass in an underground mine.

METHODS

Fossil diesel fuel was replaced with 100% HVO in all heavy trucks (EURO 5) and other non-road mobile machinery used for ore loading etc. (EURO 4 -retrofitted after -treatment) in a well-ventilated, underground mine for a period of six days.

Air quality measurements were conducted in the mobile monitoring station of THL parked at a central location of the mine 350 m below the ground level in June 2014. The campaign consisted of three 3-day intensive measurement periods (Fossil-pre, HVO, Fossil-post). (Figure 1).

Table 1. Mean (SD) values of measured pollutants using fossil or renewable (HVO) diesel fuel.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Fossil-pre</th>
<th>HVO</th>
<th>Fossil-post</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM₁₀(µg/m³)</td>
<td>160 (130)</td>
<td>120 (60)</td>
<td>120 (71)</td>
</tr>
<tr>
<td>PM₂.₅(µg/m³)</td>
<td>150 (130)</td>
<td>140 (80)</td>
<td>170 (100)</td>
</tr>
<tr>
<td>BC (µg/m³)</td>
<td>17 (3.5)</td>
<td>15 (3.9)</td>
<td>17 (3.4)</td>
</tr>
<tr>
<td>PAH (ng/m³)</td>
<td>17 (4.3)</td>
<td>14 (0.4)</td>
<td>16 (4.3)</td>
</tr>
<tr>
<td>NO₂(ppm)</td>
<td>120 (87)</td>
<td>78 (52)</td>
<td>80 (49)</td>
</tr>
<tr>
<td>CO₂(ppm)</td>
<td>710 (170)</td>
<td>680 (150)</td>
<td>720 (170)</td>
</tr>
</tbody>
</table>

PM mass and BC (diesel soot) concentrations were acceptable for work environment but comparable to heavily polluted urban traffic environments. The mean concentrations of PM mass, BC, detectable PAHs and NO₂ were about 10-20% lower during the HVO period, when compared to the means of Fossil-pre + Fossil-post periods.

Thus, the differences in air quality during the use of HVO or high-quality fossil diesel oil in modern non-road vehicles seemed relatively small.

ACKNOWLEDGEMENTS

This work was supported by the Green Mining Programme of the Finnish Funding Agency for Innovation (Tekes) and the participating companies.

REFERENCES


The origin of particles at Vavihill

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Keywords: particle number size distribution, DMPS, new particle formation, combustion

INTRODUCTION

Due to aerosol process in the atmosphere, aerosol particle properties change markedly during long range transport. Hence, it is a hard task to pin-point the sources for the number concentration of particles measured at a background field site. A combination of different analysis methods and measurement techniques are likely required to sort the source apportionment out for any field station.

One of the European long-term monitoring field sites, where the source apportionment of the particle number size distribution is tried, is Vavihill in southern Sweden.

METHODS

Several years of number size distribution data is analysed for new particle formation event days, which are among the most important sources of particles in Vavihill (Kristensson et al., 2008). Previously undefined event days are upgraded to event days with the Buenrostro Mazon (2009) method. Events at the Lille Valby site in Denmark (Wang et al., 2013) are analysed. This gives an answer if particles from events at Lille Valby have been transported to Vavihill and observed there as slightly larger particles due to condensational growth. This could give situations where we observe particles at Vavihill, which have their origin from formation, although the current day is not classified as an event day at Vavihill.

During occasions with winds from Copenhagen it is also possible to estimate the contribution from combustion generated particles.

Both methods are complemented with data from hygroscopic measurements of the water uptake at 90 % relative humidity as function of particle diameter. Water uptake might be dependent on whether there is an event taking place at Vavihill, or if there are combustion generated particles. In other words, it can potentially be used for source apportionment of particles at Vavihill.

CONCLUSIONS

We first investigated combustion generated particles. In one case-study the analysis showed that car exhaust particles from Copenhagen are able to increase the number concentration double-fold at Vavihill (Figure 1).

![Figure 1. The particle size distribution observed at Vavihill during 4 hours on February 6, 2012 for trajectories that go through Copenhagen (blue), trajectories barely missing Copenhagen (red), and the Copenhagen contribution (Through-missing).](image)

The new particle formation analysis showed that there are at least some cases when the particles observed at Vavihill are probably from formation events at Lille Valby, but not from formation at Vavihill. However, a more thorough analysis will be performed.

ACKNOWLEDGEMENTS

We acknowledge the Swedish research council FORMAS, and the study is a contribution to Lund University Strategic Research Areas: Modeling the Regional and Global Earth System (MERGE).

REFERENCES

Coastal production of new aerosol particles, for example on the west coast of Ireland, is believed to be driven by oxidation products of iodine vapors emitted by marine algae during low tide (O’Dowd et al., 2002; Huang et al., 2010). However, nucleation or cluster formation process has not been resolved in Irish coast or anywhere in the Earth’s atmosphere on molecular level. Neither has been shown, that iodine containing species drive the nucleation and initial growth, or are other species, such as sulfuric acid triggering new particle production.

To elucidate the nucleation process at the molecular level, we performed a measurement campaign at Mace Head measurement station on the west coast of Ireland. The campaign took place between 25th August and 5th October 2013.

A suite of instrumentation used to achieve this goal comprised of two Atmospheric Pressure interface – Time-of-Flight Mass spectrometers (APi-TOF): one for measuring natural ions while the other equipped with nitrate-ion chemical ionization source (CI-APi-TOF, Jokinen et al., 2012) for detection of neutral nucleating clusters and their precursors. We also utilized two particle size magnifiers (Airmodus A10) as well as Neutral cluster and Air Ion Spectrometer (NAIS) for measuring total concentration and size distributions of clusters and particles between 1.5 and 40 nm. This instrumentation is described in more detail e.g. in Kulmala et al. (2013).

Figure 1 depicts a typical coastal nucleation event observed virtually every day throughout the campaign as measured by NAIS. Here, we will report our observations on the elemental composition – measured by APi-TOF and CI-APi-TOF – of the nucleating clusters up to ~1.5 nm in diameter and up to ~2000 Th in mass. This is the first time that any atmospheric cluster formation and early growth process is resolved in elemental / molecular level.

**Figure 1. Typical coastal nucleation event as detected by NAIS.**

**References**


**ACKNOWLEDGEMENTS**

This work was supported by Academy of Finland (center of excellence project 1118615 and project 251427), the PEGASOS project (funded by the European Commission under the Framework Programme 7, FP7-ENV-2010-265148), European research council (ATMNUCLE, grant 227463) and ACTRIS.
Estimation of particle size specific infiltration of ultrafine particles in Augsburg

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Keywords: Ultrafine particles, penetration, deposition rate, infiltration, air exchange, mass-balance model

INTRODUCTION
Particulate matter (PM) has been estimated to cause substantial health losses. Specific concerns have been expressed for the ultrafine particles (Dp <100 nm). While these particles have higher relative respiratory tract deposition efficiency in the alveolar region compared with larger particles, they do penetrate into buildings and remain suspended indoors less effectively than accumulation mode particles. The aim of this work is to apply an aerosol-based model to a particle number concentration (PNC) dataset collected in Augsburg to quantify the particle size dependency of infiltration in the ultrafine particle size range.

METHODS
We have previously developed a mass-balance model for estimating PM2.5 infiltration in existing building stocks in Helsinki and reviewed similar relationships in a number of other European cities (Hänninen et al., 2004, 2011). In Helsinki we have further applied an aerosol-based particle size dependent estimation (Hänninen et al., 2013). In this work we evaluate this model on PNCs measured in Augsburg, Germany, using portable particle counters (TSI CPC 3007; Gu et al., 2014).

Measurements related to indoor environments were extracted from the personal PNC time-series using time-activity diaries. Detailed outdoor particle size distribution measurements were obtained from a fixed monitoring site representing urban background concentrations. Here the fixed site monitoring data is used together with the particle size dependent infiltration model to estimate indoor PNC, which are then compared to the observed levels.

DISCUSSION
In the infiltration process the indoor concentrations are especially lowered for ultrafine (Dp<100 nm) and coarse (Dp>1µm) sizes meanwhile the accumulation mode consisting of secondary inorganic particles is less affected by the buildings.

Here we used particle size specific outdoor concentration measurements to estimate corresponding indoor concentrations using time-windows ranging from few minutes to few hours. Due to the lack of air exchange rates or information on open windows, the accuracy of estimating indoor PNC from outdoor data was less perfect than when using the same model to estimate mass-concentrations in Helsinki.

Indoor sources (PNCin>>PNCambient) were common in the dataset and due to the study design we had no control over the indoor sources. In the current work these were filtered out from the data by using a simplified criteria (PNCi>PNCa) leaving still a small residual indoor source contribution.

The aerosol model suggests that the infiltration rate (i/o ration of outdoor originating particles) increases from below 1% at 10 nm to roughly 50% at 100 nm (Fig. 1). On log-linear scale this is almost linear. This suggests that in comparison with accumulation mode particles, exposures, and presumably doses, to ambient ultrafines must be dominated by outdoor time-activity. However, the respiratory tract uptakes have to be estimated in more detail in the follow-up.

ACKNOWLEDGEMENTS
This study was supported by the Academy of Finland Contract 133792 (PM Sizex), EU Contracts FP7-ENV-2009-1-243406 (TRANSFORM), and ENV4-CT95-0205 (ULTRA), and the participating institutes. The data collection in Augsburg was supported in part by the U.S. Environmental Protection Agency (EPA) through STAR grant RD832415 to the University of Rochester.

REFERENCES


TiO$_2$/CeO$_2$ nanocoatings synthesized by Liquid Flame Spray

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Keywords: Liquid flame spray, coatings, nanoparticles, synthesis

INTRODUCTION

Liquid Flame Spray (LFS) is an aerosol method for fabrication of nanoparticles and nanostructured coatings. LFS was used to fabricate two-component coatings consisting of TiO$_2$ and CeO$_2$ nanoparticles on various substrates. TiO$_2$ nanoparticles are known to absorb ultraviolet radiation, to exhibit photoactivity under UV exposure, and to form superhydrophobic coatings on paperboard when synthesized via LFS (Haapanen et al. 2014). CeO$_2$ nanoparticles have also been related to UV absorption (Gogarshadi et al. 2011), but their photocatalytic activity has not been very widely studied. Moreover, CeO$_2$ possesses other interesting properties, i.a. one of the highest reactivities among all rare earth oxides (Qian et al. 2011). Therefore, the addition of CeO$_2$ nanoparticles to TiO$_2$ coatings presents possibilities for a wide range of potential applications.

METHODS

In LFS process, a turbulent H$_2$/O$_2$-flame is used to evaporate atomized droplets of liquid precursor. The gaseous material reacts and nucleates into nanoparticles (primary particle size usually <50 nm), which then grow in the flame. The properties of the coatings can be controlled by variation of process parameters, such as gas flows and precursor feed and concentration. Coatings have been made on pigment-coated paperboard, glass, aluminium and stainless steel. The precursors used for fabricating TiO$_2$ and CeO$_2$ particles were titanium(IV) isopropoxide (TTIP) and cerium(III) 2-ethylhexanoate, respectively. Both precursors can be added to the same precursor solution for one-step process or layers of different materials can be deposited on top of each other separately.

CONCLUSIONS

Coatings consisting of TiO$_2$ and CeO$_2$ nanoparticles were successfully fabricated on various substrates. Figure 1 shows SEM images of a stainless steel surface before and after one-step CeO$_2$/TiO$_2$ coating. The Ce/Ti mass ratio used in the precursor solution was 3:1. Figure 2 describes the wetting behaviour of separately superimposed CeO$_2$ and TiO$_2$ coatings on paperboard after different UV irradiation times. The greater response of TiO$_2$ particles on the surface layer to the wetting implies their higher photocatalytic activity compared to CeO$_2$ particles when exposed to UV light. Various precursor feed rates were used and the lowermost layer is mentioned first. In all three cases the total mass of the metals in the coatings is equal.

Figure 1. SEM images of a stainless steel surface without (a) and with (b) LFS coating.

Figure 2. A water droplet on paperboards coated with three different parameters after various UV irradiation times.


NEW CERTIFIED OPTICAL SYSTEM FOR CONTINUOUS PM-2.5 AND PM-10 MONITORING WITH INFORMATION ON PARTICLE SIZE

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Keywords:  PM-2.5 MONITORING, PARTICLE SIZE DISTRIBUTION, CONTINUOUS AMBIENT AIR QUALITY DETECTION, ONLINE CALIBRATION STATUS

INTRODUCTION

Presented is the Fidas® fine dust monitoring system. It has just passed the requirements of EN 15267-1 & -2 for use as equivalent test method for regulatory monitoring of PM-2.5 and PM-10 in Europe. It has therefore been tested according to EN 12341, EN 14907, and the equivalency guideline at four locations over all seasons. It has also been tested at two locations in England towards MCERTS certification.

METHODS

In the course of 14 months 285 comparison data points with reference gravimetric samplers were collected and evaluated following the strict guidelines of the aforementioned standards. Data from this comparison will be presented and discussed.

Figure 1. Reference equivalency function for PM₁₀ of the Fidas® 200 S in comparison to a reference sampler in the course of performance testing taken from Report on performance testing of the Fidas® 200 S measuring system manufactured by PALAS GmbH for the components suspended particulate matter PM₁₀ and PM₂·⁵, TÜV report: 936/2121896/A

In the second part the technology and unique points will be presented in detail. While the technological basis stems from instrument development in 2000, five years of specific development regarding continuous ambient air quality monitoring preceded the equivalence and aptitude test. The Fidas® sensor
technology makes use of the approved measurement technology of optical light scattering on single particles and is equipped with a LED polychromatic light source with stable output. The scattered light intensity is detected under 90° through a patented aperture technology, thus preventing border-zone error and enabling coincidence detection. This particular approach also enables in field calibration and verification of instrument performance.

The Fidas® system operates with a volume flow of 5 l/min and is equipped with a Sigma-2 sampling head that allows representative sampling even at strong winds. It further uses an intelligent aerosol drying system (IADS) to prevent erroneous particle size classification due to moisture. It’s modular design facilitates the use in measurement stations.

CONCLUSIONS

It’s important to point out that simultaneously multiple PM-fractions (e.g. PM-1, PM-2.5, PM-4, PM-10, TSP) as well as particle number and concentration can be reported. The latter are valuable information when examining possible health implications due to inhaling aerosol particles.

REFERENCES

Report on the suitability testing of the immission measurement system Fidas® 200 S by Palas GmbH for the PM10 and PM2.5 airborne particulate matter components, TÜV report: 936/21218896/A.
Applying EXAFS for chemical speciation of zinc in fine aerosol particles from biomass combustion

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Keywords: EXAFS, Zinc speciation, Biomass combustion, Aerosol fine particles

The utilization of biomass combustion increases worldwide as a way to obtain climate neutral energy, but nevertheless causing undesirable emissions of particulate matter needed to be understood. Even if efficient combustion can be obtained, minimizing organic carbon and soot particle emissions, inorganic particles will remain. These particles consist mainly of alkali chlorides and sulfates, but also percentage levels of Zn, even though Zn is a minor trace metal in the fuel. Zn in fine particles could, depending on the speciation, cause adverse health effects and operational problems in large scale power plants. Thus, the detailed speciation of Zn in fine combustion particles is crucial, although not well investigated.

In this study, fine combustion particles (<1μm), were collected from the flue gas from a small scale (15 kW) pellet boiler. Four different fuels were investigated; softwood, wheat straw, woody energy crop, and recovered waste wood. For size fractionation a 13-stage Dekati low pressure impactor were used. Elemental composition was determined by ICP-MS/AES and the major crystalline composition by XRD. The chemical speciation of zinc was determined by using Extended X-ray Absorption Fine Structure spectroscopy, EXAFS.

The measurements were performed at the Swedish synchrotron facility MaxLab at beamline i811, a high flux photon beam for x-ray absorption spectroscopy. Data for all samples and reference compounds was collected at the zinc K-edge. The obtained data illustrates the nearest pathways between zinc as the irradiated central atom and the backscattering neighbors in the surrounding structure. Consequently, a depiction of the chemical environment around the central atom can be obtained.

The results shows that the zinc speciation dominates by two initial neighboring distances at 2.0 and 2.3 Å, suggesting a zinc oxygen distance and a zinc chloride distance respectively. Further, a second neighboring distance can be seen at 3.2 Å, known to arise from a second scattering path, generally from zinc oxide.

The results clearly indicate that the zinc speciation in the fine combustion particles is zinc chloride or zinc oxygen compounds, varying depending on the fuel. Noteworthy is also the variation at 3.2 Å concluding that the zinc oxygen distance arises from zinc oxide.

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Bio4Energy, National strategic research environment Max IV Laboratory, National synchrotron laboratory
On-line measurements of aerosol chemical composition in Helsinki city center

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Keywords: ACSM, chemical characterization, traffic related aerosols

INTRODUCTION

Aerosol chemical composition has been measured continuously from April 2013 at the Helsinki Region Environmental Services Authority (HSY) measurement station, located in Helsinki city center.

The aim of the study is to investigate seasonal differences in aerosol chemical composition in Helsinki city center. Long-term characterization of aerosol chemical composition with good time resolution gives information on the local particulate sources and how their emissions behave in various meteorological conditions. The major identified sources are traffic, wood combustion and long-range transport of pollution.

Aerosol chemical components measured in this study were sub-micrometre organics, sulphate, nitrate, ammonium, chloride and black carbon (BC). In addition, mass concentrations of PM$_{2.5}$ and PM$_{10}$ were available from the regular monitoring program of the station.

METHODS

The measurement site is located at a busy traffic environment (Mannerheimintie 5) in the city center of Helsinki. Aerosol chemical composition was measured continuously using the aerosol chemical speciation monitor (ACSM, Aerodyne Research Inc.). Black carbon was measured using the multi angle absorption photometer (MAAP Model 5012, Thermo Fisher Scientific Inc.) with PM$_1$ pre-separator. PM$_{2.5}$ and PM$_{10}$ mass monitoring was based on β-attenuation (FH 62 I-R, Thermo Fisher Scientific Inc.). ACSM measured particles <1.0 μm in diameter.

CONCLUSIONS

Measurements showed that organic matter is the most abundant aerosol component in Helsinki city center, its average mass concentration being near 7 μg/m$^3$. The average black carbon concentration was one order of magnitude lower, being on average near 0.8 μg/m$^3$. Mass concentration of organic matter showed clear diurnal variation with highest value between 19 and 20 hours. Organic matter and black carbon, which is an indicator of primary combustion particles, showed different diurnal patterns, indicating different origins (Figure 1). Mass concentration of organic matter was higher during daytime, and it started to increase in early morning hours. Higher loadings of organic matter were also observed during summer months. These indicate that secondary organic matter is at least partly photochemically produced. More detailed analyses of mass fragments of ions obtained from the ACSM measurements will give information on sources and source strengths of organic particulate matter.

The average mass concentration of sulphate and nitrate was on average 1 μg/m$^3$, and that of ammonium near 0.7 μg/m$^3$. Lower nitrate mass concentrations were measured during summer months. This is probably due to more effective partitioning of semi-volatile nitrate species in the gas phase.

Further analysis of aerosol sources in Helsinki city center will be made based on aerosol chemical and physical measurements using statistical tools like factor analysis.

![Figure 1. Diurnal variation of total organics (left axis), and of black carbon (right axis) between April 2013 and October 2014.](image)

ACKNOWLEDGEMENTS

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Effect of ageing on chemical composition of log wood combustion aerosols: aerosol mass spectrometer study

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Keywords: wood combustion, aerosol, ageing, AMS

INTRODUCTION

Emissions from small-scale wood combustion have worldwide a substantial contribution to the ambient air particulate matter levels, producing especially large amount of submicron black carbon (BC), primary organic aerosols (POA) and secondary aerosols.

The secondary aerosols are formed via the oxidation of gas-phase organic emissions (secondary organic aerosols, SOA) and oxidation of NOx to NO3.

METHODS

The Kuopio HICE campaign was conducted at ILMARI, a multidisciplinary research unit for combustion aerosol physics, chemistry and toxicology, in the University of Eastern Finland in October 2013. Atmospheric aging processes of log wood combustion aerosols were studied both in an environmental chamber, equipped with adjustable UV lights (total 160 blacklight lamps) (Leskinen et al., 2014) and in a photo-oxidation flow chamber (PAM) simulating conditions ranging from hours to several days in atmosphere.

The soot particle aerosol mass spectrometer (SP-HR-ToF-AMS, Aerodyne Research Inc.), equipped with a laser vaporizer, was applied to determine the major fraction of combustion aerosols including numerous refractory compounds e.g. refractory black carbon (rBC).

CONCLUSIONS

Formation of SOA by photo-oxidation in PAM chamber increased OA mass when UV light was switch on. HR-AMS results showed high O/C ratios with CO₂⁺ as main fragment especially when Nd: XG -laser vaporizer was applied. Photo-oxidation (UV on) in PAM chamber elevated C₃H₂O⁺ signal, more than CO₂⁺, indicating a higher ratio of non-acid oxygenated OA compounds in aged wood burning OA compared to fresh emissions (Fig 1, Elsesser et al., 2012). Effect of thickness of aerosol coating on OA oxidation is under investigation.

Figure 1. Refractory black carbon (rBC) concentration and oxygenated OA ions, C₃H₂O⁺ (less oxid.) and CO₂⁺ (more oxid.) variations after ageing in PAM flow reactor during six batches (1-6, dashed lines) of beech log wood (modern masonry heater). UV light was off during batch 4. Ozone concentration is also presented.

ACKNOWLEDGEMENTS

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Chemical characterization of primary and secondary aerosol in flexible-fuel engine emissions


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Keywords: Aerosol chemistry, secondary aerosol, traffic emissions

INTRODUCTION

Vehicular emissions are known to degrade air quality in urban areas. Besides gaseous compounds (e.g. CO, NOx, hydrocarbons), vehicle exhaust contains significant amount of primary particulate matter. In addition, large amounts of secondary particulate matter form after the exhaust gases are released into atmosphere. Secondary PM emissions from traffic and their influence to air quality are not well known. Recent studies using smog chamber have shown that the secondary organic PM emissions can be up to 10 times larger than primary emissions if conditions are optimal for secondary aerosol formation (Chirico et al., 2010). In this study primary and secondary particulate emissions from two vehicles with different flexible-fuel engines were measured using new European driving cycle (NEDC) in order to characterize chemical composition and size distributions of primary and secondary particulate emissions.

METHODS

Particulate emissions from two passenger cars (VW Passat MultiFuel, DISI engine, Ford Mondeo 2.0 FlexFuel, natural aspirated MPI engine) using fuels with different alcohol content (E10, E85, E100) were measured with chassis dynamometer at the engine laboratory. Aerodyne Soot Particle Aerosol Mass Spectrometer (SP-AMS, Onasch et al., 2012) was used to measure size-resolved chemical composition of submicron non-refractory particulate matter, refractory black carbon and some metals and elements. A Potential Aerosol Mass (PAM) chamber was used to study secondary aerosol formation. PAM chamber is a small, flow-through reactor in which oxidants (O3, OH-, and HO2) are formed from UV light.

CONCLUSIONS

All driving cycles were performed with and without the PAM chamber, which enabled characterization of primary (no PAM chamber) and secondary (added aerosol mass with PAM chamber) fractions of the particulate emissions. Primary particulate emissions consisted mainly of hydrocarbons and black carbon. Largest primary particulate emission concentrations were measured for E10 fuel. Secondary particulate emissions were mainly highly oxidized organic compounds and nitrate. With PAM higher O:C –ratios and lower H:C –ratios were observed when compared to measurements without PAM. As the amount of alcohol increased in the fuel (E85, E100) a significant decrease in primary particulate emissions and a decrease in secondary aerosol formation was observed.

ACKNOWLEDGEMENTS

This work was supported by the Academy of Finland (Grant No. 259016), Helsinki Energy, Ministry of Traffic and Communications and TEKES in the CLEEN/MMEA programme (WP4.5.2). Chassis dynamometer measurements were carried out within the IEA’s Implementing Agreement on Advanced Motor Fuels (AMF) as Annex 44 (http://www.iea-amf.org/content/projects/annexes/44).

REFERENCES

Explicit representation of subgrid variability in cloud microphysics yields weaker aerosol indirect effect in the ECHAM5.5-HAM2 climate model

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Keywords: Aerosol indirect effects, subgrid parameterizations

INTRODUCTION

Aerosol-cloud interactions and their changes due to anthropogenic aerosol emissions represent a major uncertainty in climate projections. While the uncertainty range for the indirect aerosol forcing is still large in general, models tend to produce considerably stronger indirect forcing than the best estimate based on expert judgment and satellite studies. In this work, a stochastic subcolumn framework (Räisänen et al. 2004; Tonttila et al. 2013) for clouds and radiation implemented in the ECHAM-HAM climate model is used to estimate the effects of anthropogenic aerosols on cloud properties and radiation.

METHODS

The ECHAM5.5-HAM2 climate model has been augmented with a subcolumn framework, where realizations of the subgrid cloud macro- and micro-physical structure are generated based on statistical information resolved in the model. The subgrid cloud properties are then self-consistently applied to radiative transfer using the Monte Carlo Independent Column Approximation method (Pincus et al. 2003).

The aerosol indirect effects are investigated by running simulations in pre-industrial (PI) and present-day (PD) emission conditions using model configurations with and without subgrid variability in the cloud microphysics.

CONCLUSIONS

The main results from this work are:

1. Subgrid treatment of cloud activation decreases cloud droplet number concentration (CDNC) both in PI and PD conditions. Even further decrease in CDNC and a clear reduction in LWP take place when also autoconversion is calculated in the subcolumn space. Globally, the subgrid parameterizations yield only a moderate decrease in the PI-PD change of CDNC, although locally a more significant impact is seen in the northern mid-latitudes.

2. With subgrid cloud microphysics, an anthropogenic increase in the aerosol number concentration increases the spread in the subgrid CDNC distribution, which tends to increase the autoconversion rate relative to the grid-mean calculation. Thus, the LWP change between PI and PD simulations is reduced by up to 19\% in the global mean.

3. The direct impact of subgrid cloud microphysical parameterizations is to decrease the model estimate of the indirect radiative effect of aerosols by 19\%, as compared to the reference model where cloud microphysics are considered in the climate model grid-scale. The new model version must be retuned to account for the large difference in the global mean radiative balance, as compared to the reference model configuration. After retuning, the reduction in the indirect aerosol effect is 14\%, which is still significant and more closely resembles the impact of the subgrid parameterizations in an operational setup.

ACKNOWLEDGEMENTS

This work was supported by a Väisälä foundation grant from the Finnish Academy of Science and Letters and by the Academy of Finland (project numbers 127210, 283030).

REFERENCES


Day- and night-time composition and morphology of aerosol samples from polluted air

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Keywords: air pollution, chemical composition, morphology

INTRODUCTION
China has encountered air quality problems because of rapid industrialization. Mixed emissions of energy production, traffic, industry, construction and traditional agricultural combustion can simultaneously occur in the air. Particulate and gaseous pollutants cause shortening of life expectancy. The mechanisms through which the particulate pollutants cause adverse health effects are partly connected to their chemical composition and morphology. In this study the day- and night-time variation of chemical composition, size and morphology of air samples collected from NJU station, Nanjing, China (Fig. 1), were studied.

METHODS
The particulate samples were collected with a high volume cascade impactor (HVCI). The collected PM was analyzed for chemical composition using ion chromatography, ICP-MS and GC-MS for the determination of inorganic anions, metals, as well as PAH compounds. The samples for TEM analysis were collected during daytime only. The analyses were performed using JEOL JEM-2100F at 200 kV acceleration voltage.

RESULTS AND CONCLUSIONS
The nitrate and sulfate were the largest components of the PM. The nitrate level increased at night and, vice versa, sulfates during the day (Fig. 2). Moreover, phosphates were detected only from the daytime samples. From the measured elements some metals, including Zn, K, Fe, Ca, and Al, had substantial proportions. The determined Cl⁻ content was larger in the night-time collected samples than during the day. Some of the analyzed elements, e.g. Al and Ca, were clearly enriched in the PM₁₀⁻₁·₅.

Sulfate rich particles of multiple size were most frequently observed in the TEM analysis. These particles most probably contain particulate material from multiple sources. Internal mixture of sulfates with soot, metal particles (Fig. 2), organics and salts were observed. Fe was found in all size fractions as small (< 10 nm) spherical particles and clusters. It is suggested that Fe-rich nanoparticles were origin of industrial activity, such as a metal smelter plant, in accordance with previous studies (Li & Shao 2009).

The findings indicate that both the local sources of emissions and secondary aerosols formation have large effect on the composition and morphology of the PM.

ACKNOWLEDGEMENTS
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REFERENCES
In vitro toxicology studies on PM samples collected from urban air in wood combustion area

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Keywords: ambient air, in vitro, cytotoxicity, genotoxicity, wood combustion.

INTRODUCTION

A long term ambient air particulate matter (PM) characterization and source apportionment work has been carried out in Grenoble area, France, since 2006. Biomass burning tracers as well as regulated atmospheric pollutants have been sampled and analysed in Grenoble by the corresponding air quality network (“AIR Rhône-Alpe”) and French university laboratories (LCME, LGGE). According to different mono and multi tracer approaches, biomass burning contribution has been estimated to be 41% from PM₂.₅. The aim of the present study was to investigate health related toxicological characteristics of urban air particulate samples in Grenoble and their relationship to physicochemical properties of the same samples in vitro.

METHODS

PM₁ collection was performed during January and February 2011 in an urban site located in the Grenoble north area. Sampling instrument was set up in a high population density neighbourhood. PM₁ samples used for chemical and toxicological analyses were collected using a High Volume Sampler (HVS: DA-80) provided with a cut head at 1 µm and running at a 30 m³/h flow rate. Tracer approaches including levoglucosan (levo) were used to evaluate the amount of wood combustion contributed to PM₁.

PTFE membrane filters were used for the PM₁ collection. The filters containing collected particulate material were cut into pieces and eluted with methanol in an ultrasonic water bath two times 30 min at a temperature below +35 °C. Three PM₁ samples were gained Low-levo, Mid-levo and High-levo. Mouse macrophage cells (RAW264.7) were exposed for 24 h to four doses (15, 50, 150 and 300 mg ml⁻¹) of those samples.

The total amount of propidium iodide (PI) positive cells with a lowered cell membrane potential was detected by flow cytometry. DNA damage was assessed by the comet assay.

RESULTS

Figure 1. RAW264.7 macrophages were exposed for 24 h to the three different ambient air samples. Cytotoxicity was evaluated using the propidium iodide (PI) exclusion test. Each whiskers represent the standard error of mean (SEM). The asterisks indicate statistical significance compared to control (p < 0.05) analyzed by non-parametric Kruskal-Wallis test.

Figure 2. Genotoxicity assessed with comet assay after 24 h exposure to PM₁ from different ambient air samples. Bars represent three doses (50, 150 and 300 mg ml⁻¹) and whiskers the standard error of mean (SEM). Asterisks indicate statistical significance compared to control (p < 0.05) analyzed by non-parametric Kruskal-Wallis test.

CONCLUSIONS

In this study, all particulate samples increased cell death in a dose-dependent manner in the PI-exclusion assay. The most extensive cytotoxic responses were detected after cells exposure to the samples which had highest concentration of levoglucosan. Same trend was seen in genotoxic effects. Local combustion emissions contribute a lot to the inhaled particle fraction of fine particles in real-life. The present data suggest that the harmfulness of ambient particles is enhanced when there are local wood combustion sources present.
Hygroscopic properties of interstitial particles and cloud droplet residuals: Preliminary results from the PuCE 2014 field campaign

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Keywords: aerosol-cloud interactions, aerosol hygroscopicity

INTRODUCTION

In order to understand better the processes governing atmospheric aerosols, clouds and their interactions, we carried out an intensive measurement campaign (PuCE 2014) at the Puijo SMEAR IV station (e.g. Leskinen et al., 2009) during the autumn 2014.

Besides the stationary measurement instruments, the station was equipped with an Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), hygroscopic tandem differential mobility analyzer (HTDMA), cloud condensation nuclei counter (CCNC) and proton transfer reaction time-of-flight mass spectrometer (PTR-ToF). In this abstract we present the preliminary results concerning the conducted HTDMA measurements.

EXPERIMENTAL

The HTDMA was operated to measure the hygroscopic growth factors (GF) at dry diameters of 80, 120 and 150 nm. The relative humidity applied in the humidifier was approximately 90% and the instrument was permanently attached to the total air inlet.

For a four-week period, we also utilized the custom made twin inlet system (Portin et al., 2014) in order to measure the total air (TOT) and interstitial particles (INT) separately. During a cloud event, the total air inlet sucks in all the particles and cloud droplets with cut-off diameter of 40 µm. Meanwhile, the interstitial sample flow (PM1.0) contains only the non-activated particles.

PRELIMINARY RESULTS

During the campaign, the measured growth factors varied between 1.03 and 1.75, reaching the campaign averages (± one standard deviation) of 1.36 ± 0.11 (80 nm), 1.47 ± 0.10 (120 nm) and 1.51 ± 0.09 (150 nm).

Figure 1 shows the average GFs and GF-PDFs (probability density functions) for different sampling lines and dry sizes during the observed cloud events. Since the 80 nm particles do not usually activate into cloud droplets, the measured aerosol population is almost the same for both sample lines. However, the 120 and 150 nm particles are already showing distinctive differences between different populations, with interstitial particles appearing less hygroscopic than the activated ones.

This was one of the first attempts to measure the hygroscopicity spectra of total and interstitial aerosol separately in natural, atmospheric conditions. In the near future, the aim is to utilize these results in order to study the relationship between aerosol hygroscopicity and cloud condensation nuclei activity in more detail.

ACKNOWLEDGEMENTS

This work was supported by Academy of Finland Centre of Excellence (decision no. 272041).

REFERENCES


Figure 1. Average GFs and GF-PDFs during cloud events for dry diameters of 80, 120 and 150 nm. The numbers given in the legends correspond the number of individual HTDMA data points used in the averaging.
1-3nm particles detected in urban air

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Keywords: nucleation, urban air, engine, emission

INTRODUCTION

Atmospheric particle nucleation has been proven to take place also in polluted urban environments (Qian et al., 2007). In addition to the secondary particle formation there are other sources of nano-sized particles in urban air; e.g. vehicle emissions contain not only numerous ultrafine particles, but also small aerosol particles of the order of possibly just a few nanometers in diameter (Keskinen & Rönkkö, 2010). Sub 10 nm and even sub 3 nm particles are likely detectable in the vicinity of other ambient combustion sources as well.

METHODS

We have developed, together with the University of Helsinki, a nano Condensation Nucleus Counter (nCNC) system for the measurement of the number size distribution of 1-3 nm particles (Kulmala et al., 2012; Vanhanen et al., 2011). The nCNC system was originally developed for ambient nucleation studies, and it has been used for field studies in different environments. The nCNC uses diethylene glycol vapor to activate and grow particles as small as 1nm in diameter. The particle size distribution up to 3nm can be measured by varying the flows and eventually the supersaturation of the nCNC system. One size spectra can be achieved in 4 min time. We will present an overview of some of the findings so far and discuss the application of the system in urban environment. We will present data measured in an urban background site SMEAR III in Helsinki Finland. Both urban background and roadside data will be shown.

CONCLUSIONS

New particle formation was measured in urban environment in Helsinki. Figure 1 shows both DMPS and nCNC data from SMEAR III station in 1st of June 2014. DMPS data shows that new particles in sizes starting well below 10nm can be observed starting at noon. Clear growth of the newly formed particles can be seen from the figure. At the same time nCNC detects small clusters below 1.5 nm. The nCNC data also shows growth of the clusters.

Combustion-generated particles were detected in size range of 1-5nm in diameter from a roadside measurement site at the SMEAR III station. The data shows clear variation of the particle concentration as a function of bus traffic.

Both data sets show that sub 3 nm particles can be measured in urban environment and that the sources can be both engine emissions and secondary new particle formation.

REFERENCES

Effects of humidity conditions on hygroscopicity of freshly nucleated particles

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Keywords: HTDMA, Hyytiälä, new particles, hygroscopicity

INTRODUCTION

Hygroscopicity, the ability of particles to take up water, is one of the important factors that determine the number of cloud condensation nuclei and further affect the lifetime of the clouds. There are a large number of studies which have measured hygroscopicity of submicrometer aerosol particles in various environments around the world (Swietlicki et al., 2008). However, how the varying humidity conditions will affect the aerosol hygroscopicity remains unknown. This study aimed to provide insights into this scientific question by field measurements.

METHODS

Measurements for this study were conducted in a boreal forest in Finland by using a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA). More descriptions of the experimental campaign are summarised in Table 1.

<table>
<thead>
<tr>
<th>Sampling Location</th>
<th>Hyytiälä, Finland</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling Period</td>
<td>10 Apr – 29 May, 2014</td>
</tr>
<tr>
<td>Instrumentation</td>
<td>HTDMA</td>
</tr>
<tr>
<td>Time Resolution</td>
<td>30 min</td>
</tr>
<tr>
<td>Particle Size Selected</td>
<td>30 nm, 50 nm</td>
</tr>
<tr>
<td>Humidity Conditions</td>
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</tr>
</tbody>
</table>

CONCLUSIONS

Over ten nucleation events were observed during the measurement period, but only the data collected in 15-17 Apr, 2014 are presented here as an example.

The main results are as follows: (1) during the new particle formation event, no differences in hygroscopicity measurement (i.e. hygroscopicity parameter κ) at different RH; (2) after growth (i.e. during night hours), hygroscopicity decreases with increasing humidity; and (3) lower κ values were observed at higher relative humidity, which follows the trend recently observed for laboratory generated SOA (Pajunoja et al., 2014).

Particle composition analysis is still in progress, and its results will help us to explain the hygroscopicity behaviors.

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REFERENCES

Insights Into the Microscopic Surface Composition of Succinic Acid in Aqueous Solutions

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Keywords: XPS, surface activity, MD, dicarboxylic acids, aqueous surface, partitioning, surface tension
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INTRODUCTION

Some of the inorganic and organic compounds that are identified in atmospheric aerosol particles are known to have either positive or negative surface propensity in aqueous solutions. Hence, the concentration and composition of the surface is generally rather different from the bulk. In an extreme case, enhancement of one species may lead to depletion of another. As the surface fraction increases with decreasing aerosol size, surface effects become increasingly important for small systems, such as droplets and aerosol particles in the atmosphere. There is a need to qualitatively explore these surface phenomena and to quantify the effects for specific environmentally important compounds.

METHODS

Our main tool to probe aqueous solutions is core-level X-ray Photoelectron Spectroscopy (XPS) on a liquid micro-jet using synchrotron radiation. The key advantages of core-level spectroscopy are that both the chemical state and the microscopic spatial distribution of the component species are probed. Hence, our results provide information on how the surface composition of atmospherically relevant aqueous systems varies with parameters such as bulk composition, pH, concentration and co-solvation.1-3 Results can be complemented with molecular dynamics (MD) simulation and compared to changes in thermodynamic quantities, e.g., surface tension, vapor pressure, etc.

RESULTS & CONCLUSIONS

Results from aqueous solutions containing succinic acid and mixtures of these with inorganic salts will be presented. More specifically, results of a XPS study on different concentrations of succinic acid, which are supplemented with MD simulations, are compared and discussed together with surface tension models and measurements. The results reveal the microscopic surface composition and speciation. Using a simple model, as depicted in Figure 1, surface concentrations are estimated. Furthermore, we recently studied the surface composition of aqueous solutions of succinic acid in mixtures with inorganic salts, such as sodium chloride or ammonium sulfate. The change in surface concentration is investigated as function of the known bulk concentrations, added inorganic salt and pH. From the results a range of surface enrichment factors of the organic are derived.

Figure 1 Simple schematic on succinic acid and sodium succinate solutions. Succinic acid is strongly enhanced while the divalent succinate ions avoid the water-air interface.

REFERENCES

Heterogeneous Ice Nucleation on Biological and Mineral Dust Particles
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Keywords: heterogeneous ice nucleation, immersion freezing, bacteria, pollen

INTRODUCTION
Heterogeneous ice nucleation processes play a significant role in the formation of precipitation in mid-latitudes, influence the radiative properties of clouds, and hence have effects on both, weather and climate. Despite intense research in the past decade, the fundamental workings of heterogeneous ice nucleation as well as the relative importance of different substances in atmospheric ice nucleation are still poorly understood. Mineral dust has been thought to be an important ice nucleating component, however recent findings (e.g. Pummer et al., 2012; Hartmann et al., 2013; Augustin et al., 2013) suggest that biological macromolecules, even if detached from their original carrier, may play an important role.

METHODS AND RESULTS
To investigate heterogeneous ice nucleation processes, at TROPOS the Leipzig Aerosol Cloud Interaction Simulator (LACIS) is utilized (Hartmann et al., 2011). Basically, LACIS is a 7m long laminar flow tube, equipped with sophisticated techniques for ice nucleating particle (INP) generation and characterization, as well as means for hydrometeor sizing and phase discrimination. For the investigations presented here, we considered the immersion freezing of similar sized droplets, containing single size selected monodisperse INP, generated from mineral and/or biological material. Specifically we investigated the ice nucleation behaviour of feldspar, different clays as well as pollen and bacteria. As examples for the results and insights gained, Figure 1 depicts ice fractions for pure and sulphuric acid coated mineral dust particles (left and middle panel, respectively, Augustin-Bauditz et al., 2014), and the INP size distribution for the investigated bacteria (Pseudomonas syringae from Snomax).

Figure 1: Ice fractions (left and middle panel) as function of temperature, and INP size distribution (right panel)

Figure 1 underlines the main results of the investigations performed, which are: We derived a base line for ice nucleation of clays, and found feldspar to be more ice active than clays; single biological macro molecules can nucleate ice even when separated from their original carrier (e.g. bacteria or pollen grain); a population of mixed mineral-biological particles features both the biological and the mineral ice nucleation behaviour.

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Cloud droplet activity measurements of coated soot particles

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Keywords: CCN, soot, organics, SFCA

INTRODUCTION

The ability of soot particles to act as cloud condensation nuclei (CCN) and affect the hydrological cycle of Earth will improve after atmospheric processing. Both anthropogenic and biogenic sources may contribute to the change in particle properties via complex gas-to-particle conversion processes. Highly time resolved experimental measurements in combination with continuous atmospheric measurements are required to improve the understanding of the changing hygroscopicity of the processed soot particles.

METHODS

Here, we present results from measurements with the Cloud Condensation Nuclei Counter (CCNC, DMT-100) running in Scanning Flow CCN Analysis (SFCA) operational mode (Moore and Nenes, 2009). The technique induces a change in supersaturation by changing the flow through the column while keeping the temperature gradient and pressure constant. SFCA has been tested in laboratory experiments as well as in ambient measurements at urban and rural locations. In the laboratory experiments the primary aerosol included soot produced from two different sources: (i) a Euro II Diesel Passenger Vehicle and (ii) a diffusion flame soot generator. Thereafter, anthropogenic or biogenic precursors were added to the aerosol and photo-chemically or chemically aged to enable condensation of secondary organic aerosol (SOA) onto the soot particles. In short for all measurements, the aerosol has been size-selected using a differential mobility analyser in front of the CCNC. The aerosol has been characterised elsewhere (e.g. urban, Rissler \textit{et al.}, 2014; anthropogenic, Wittbom \textit{et al.}, 2014).

CONCLUSIONS

Results show a decreasing critical supersaturation ($s_c$) with increasing amount of SOA, independent of precursor. The $s_c$ determines the point of activation of the particles into cloud droplets (Fig. 1). Using SFCA requires small samples and/or entails a high temporal resolution of the CCN spectra ($\leq$5 min).

A size-dependency according to the mobility diameter ($d_m$) was observed (Fig. 2; colour code). The volume equivalent diameter ($d_v$), calculated from the particle mass-mobility relationship, approach $d_m$ as the ageing progress, indicating a change in morphology. Also, particles with different primary particle diameter ($d_{pp}$) show slight difference in $s_c$ for a given $d_v$, (compare red (2) with turquoise (1&3) in Fig. 2).

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REFERENCES

Role of particle phase processes and uptake of low-volatile organic compounds - Modelling study on nanoparticle growth

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Keywords: nanoparticle growth, condensation, organic aerosol, new particle formation

INTRODUCTION

The growth of atmospheric secondary aerosol particles, nanoparticles, is mainly due to uptake of organic and inorganic trace gases. In many environments organic compounds formed in the oxidation of volatile organic compounds (VOC) are the major contributor to the growth. Only low-volatile organic compounds are expected to contribute to the nanoparticle mass significantly. These low-volatile compounds can be formed in the gas phase, at the particle surface or in the particle phase. Thus, uptake of organics by nanoparticles can be divided into two: condensation of low-volatile organic compounds (LVOC) formed by gas phase oxidation and condensation of semi-volatile organic compounds (SVOC) followed by subsequent production of low-volatile compounds in the particle (Riipinen et al., 2012).

The aim of this study is to identify the groups of organic compounds and the processes that are important for atmospheric nanoparticle growth. The focus is on the four processes considered to be especially important for nanoparticle growth: particle phase salt formation, particle phase oligomerization, uptake of low-volatile gas phase oxidation products and particle phase diffusion. These processes likely take place simultaneously and have varying importance along the particle growth (Riipinen et al., 2012) and possibly also affect each other. In this study we develop and utilize a numerical model for simulating nanoparticle growth and compare the roles of various compounds and processes in the growth.

METHODS

In this study we use new particle growth model KM-GAP-T for studying the nanoparticle growth. KM-GAP-T combines of two previously developed models: KM-GAP which is a kinetic multi-layer model with detailed representation of mass fluxes in and between gas phase, particle surface and particle bulk (Shiraiwa et al., 2012), and MABNAG which is a particle growth model with particle phase acid-base chemistry. KM-GAP-T (KM-GAP with thermodynamics), has similar layer approach and treats the oligomerization similarly as KM-GAP, while acid-base chemistry and composition dependence of equilibrium vapor pressures are calculated with E-AIM (Clegg & Seinfeld, 2006) and condensation of water and ammonia is calculated assuming equilibrium between gas phase and particle surface layer following the approach of MABNAG.

CONCLUSIONS

Using the model we show that, depending on their thermodynamic and kinetic properties, the semi-volatile organic compounds may contribute to the atmospheric nanoparticle growth due to their participation in particle phase processes (oligomerization and salt formation). However, especially at the smallest particle sizes uptake of low-volatile organic compounds is important.

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REFERENCES

What is the effect of green leaf volatiles on SOA formation?

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Keywords: herbivore-induced plant volatiles, green leaf volatiles, secondary organic aerosol, deciduous tree

INTRODUCTION

Insect herbivores feeding on plant leaves act as biotic stressors and induce specific emission profiles of volatile organic compounds (VOCs) (Holopainen & Blande, 2013). These reactive VOCs, including the so-called GLVs, green leaf volatiles, may undergo various oxidation and condensation processes in the atmosphere which leads to formation of secondary organic aerosol (SOA). However, the role of GLV compounds in SOA formation is debated: there is evidence showing that these compounds could have a suppressive effect on SOA formation (Mentel et al., 2013), but opposite results suggesting that GLV compounds can be a substantial source of SOA have also been reported (Hamilton et al., 2009; Harvey et al., 2014). Still, the overall effect of insect outbreaks may promote SOA formation due to the emission of these reactive VOCs from boreal and subarctic forests (Mentel et al., 2013).

In the current study we measured the impact of herbivore (autumnal moth, Epirrita autumnata) damage on mountain birch VOC emissions under laboratory conditions, and observed their capacity for SOA formation. The second part of our experiment consisted of experiments with pure GLVs to observe their SOA forming potential.

METHODS

We performed two sets of chamber experiments, first one to elucidate the effects of herbivory on mountain birch emissions and concurrent SOA formation by ozonolysis. In the second chamber experiment series we tested three main green leaf volatiles: (E)-2-hexenal, (Z)-3-hexenol and (Z)-3-hexenyl acetate to reveal their effect on SOA formation processes. VOC concentrations were measured by thermal desorption cold-trap GC-MS and PTR-TOF-MS systems. Particle formation and growth events were monitored with a scanning mobility particle sizer.

CONCLUSIONS

First set of experiments clearly showed that the deciduous tree seedlings damaged by herbivore had a higher capacity for SOA formation when compared with intact seedlings. The results provide conclusive evidence that the quantitative and qualitative changes in VOC emissions of mountain birch after herbivory are sufficient to promote secondary aerosol formation. In these experiments, GLV emissions dominated the VOC composition in the herbivore-damaged samples whereas they were almost absent in the control experiments. It seemed thus likely, that the GLVs were the main causative reactants in SOA formation. However, we wanted to test this hypothesis.

In the second set of experiments we tested GLVs individually and together with selected monoterpenes from mountain birch emission. When tested with any of the monoterpenes, the presence of GLVs suppressed the SOA formation in relation to the SOA formation caused by oxidation of the monoterpenes alone. Simultaneously, we observed lower proportion of the condensable monoterpene oxidation products in the GLV + monoterpene experiments. It is therefore possible that GLVs compete with monoterpenes to react with the oxidative compounds, resulting in suppressed SOA formation.

Our results suggest that herbivore action could significantly increase the reactive VOC emissions that can importantly contribute to SOA formation in subarctic forests. Even though the GLVs likely suppress the SOA formation, the rather modest increase in mono- and sesquiterpenes, along with the other reactive herbivore-induced plant volatiles, is sufficient to trigger SOA formation processes in the atmosphere.

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Relating Aerosol Properties to Cloud Microphysics Observed during the ACCACIA Campaign: An ESEM/EDX Study

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Keywords: Arctic, ACCACIA, cloud microphysics, ESEM/EDX

INTRODUCTION

Our ability to comprehend and climatologically model the polar regions of our planet is currently hindered by a lack of observations of the atmospheric processes unique to these regions. A significant contributing source of uncertainty to these models may be found in our representation of aerosol-cloud interactions (e.g. Curry et al., 1996).

The properties of Arctic aerosol and their ability to nucleate ice are of key importance, as there are unanswered questions regarding how the concentrations of these unique particles correlate with the cloud microphysics of this region (e.g. Prenni et al., 2009).

METHODS

In an effort to address this issue, the Aerosol-Cloud Coupling and Climate Interactions in the Arctic (ACCACIA) campaign was conducted in the vicinity of the Svalbard archipelago, carrying out in-situ airborne observations of the mixed-phase clouds in this region. This campaign was carried out in two segments during the spring and summer of 2013, with airborne- and surface-based measurement platforms utilised in each. During the spring campaign, a wide range of microphysics probes were active on board the FAAM BAE146 aircraft. For example, contributions from the Two-Dimensional Stereoscopic (2D-S) Probe, the Cloud Droplet Probe (CDP) and the Passive Cavity Aerosol Spectrometer Probe (PCASP) will be included to provide a detailed insight into the aerosol and cloud properties observed during this section of the campaign.

To contribute towards a thorough investigation of the aerosol and cloud microphysical properties of the polar atmosphere, polycarbonate filters were also exposed from the FAAM BAE146 aircraft during the spring segment of the campaign. This collection technique produces in-situ samples of the coarse-mode Arctic aerosol that may likely be acting as Ice Nuclei (IN) in the region. The compositional and morphological properties of these particles have been investigated using an Environmental Scanning Electron Microscope with Energy-Dispersive X-Ray Spectroscopy (ESEM/EDX). This technique allows the elemental weight content of each particle to be quantified, and so the particles’ composition may be inferred. This analysis can therefore provide an insight into the physical properties of these coarse-mode, non-volatile aerosol that may be facilitating ice crystal growth in the Arctic atmosphere.

Relationships between data from the filters and the optical particle counters on board the aircraft will be presented. For example, the investigation will include comparisons between the absolute mass-size distributions deduced from the filtered particles and the corresponding data from the aircraft to provide an indication of which aerosol properties may be influencing the ice crystal concentrations in the springtime Arctic clouds observed.

CONCLUSIONS

The ice crystal concentrations were found to vary little across the spring campaign, whilst the composition of aerosol collected was markedly distinct between individual flights. Significant fractions of sea salts, silicon-based and/or calcium-based dusts were identified in a number of cases, suggesting that a variety of natural sources may yet be influencing the microphysics of the Arctic atmosphere from a distance.

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REFERENCES

Composition and biological effects of aerosols from ship diesel engine and wood combustion compliances: Joint analysis of aerosol properties and the molecular biological effects on human lung cells

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INTRODUCTION

Ship engine emissions are important regarding lung and cardiovascular diseases in coastal regions worldwide. Bio mass burning is made responsible for adverse health effects in many cities and rural regions. The Virtual Helmholtz Institute-HICE (www.hice-vi.eu) addresses chemical & physical properties and health effects of anthropogenic combustion emissions. Typical lung cell responses to combustion aerosols include inflammation and apoptosis, but a molecular link with the specific chemical composition in particular of ship emissions has not been established.

METHODS

We exposed human lung cells to exhaust fumes from a ship engine running on common heavy fuel oil (HFO) and cleaner-burning diesel fuel (DF) as well as to emissions of wood combustion compliances by an air-liquid interface exposure system (ALI). A special field deployable ALI - exposition system and a mobile S2-biological laboratory were developed for this study. Human alveolar basal epithelial cells (A549 etc.) were ALI-exposed to fresh, diluted (1:40-1:100) combustion aerosols and subsequently toxicologically and molecular-biologically characterized. Advanced chemical analyses of the exhaust aerosols were combined with transcriptional, proteomic and metabolomic profiling to characterize the cellular responses.

CONCLUSIONS

The HFO ship emissions contained high concentrations of toxic compounds (transition metals, organic toxicants) and high particle mass. The cellular responses included inflammation and oxidative stress. Surprisingly, the DF ship emissions, which predominantly contain rather “pure” carbonaceous soot and much less known toxicants, induced significantly broader biological effects, affecting essential cellular pathways (e.g., mitochondrial function and intracellular transport). Therefore the use of distillate fuels for shipping (this is the current emission reduction strategy of the IMO) appears insufficient for diminishing health effects. The study suggests rather reducing the particle emissions by secondary measures (filters) than shifting the fuel. In the case of wood combustion the reduction of soot and carcinogetic aromatic compounds is suggested. Furthermore, the shipping emissions are compared to the emission of different wood combustion compliances.