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MODELLING AEROSOL FORMATION AND PRECURSOR  
GASES IN THE BOUNDARY LAYER

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Academic dissertation

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# Modelling aerosol formation and precursor gases in the boundary layer

Luxi Zhou

University of Helsinki, 2015

## Abstract

Aerosols are common air pollutants that pose serious threats to health. They also impact the Earth's climate by interacting with solar radiation and altering cloud properties. One important phenomenon associated with the atmospheric aerosol system is new particle formation. This thesis is devoted to study the processes related to new particle formation as well as aerosol precursor gases in the boundary layer, where exchanges between the surface and the atmosphere take place.

Model SOSAA, a one-dimensional transport model with detailed chemistry and aerosol microphysics, was constructed, tested and used as the main tool. Variations in the main biogenic volatile organic compounds (BVOCs), OH and H<sub>2</sub>SO<sub>4</sub> across different environment were analysed. The simulated concentrations of main emitted organic compounds in two rural sites agree well with the observations. Due to missing OH reactivity in rural environment, the concentration of OH at Hyytiälä is overestimated. In contrast, the concentration of OH is likely underestimated in an urban environment due to missing production from HONO. H<sub>2</sub>SO<sub>4</sub> production is underestimated at every site studied. New particle formation was studied in two phases: nucleation and growth. Large uncertainties are introduced to nucleation rates when calculating dependencies based on sulphuric acid alone. The oxidation products of monoterpenes by OH are shown not to be a suitable proxy for nucleation at either the urban site in Beijing or the rural site at Hyytiälä in summer. While they mainly contribute to the growth of particles at the rural site in Hyytiälä, the oxidation products of monoterpenes might only have major role in particle growth at Manitou during the evening. The rapid particle growth at Manitou in the daytime is possibly related to the oxidation products of 2-Methyl-3-Buten-2-ol (MBO) by OH or any compound that has similar concentration and diurnal variation to the oxidation product of MBO by OH. The last model study assessed the climatic impact of aerosols in a hypothetical scenario with high atmospheric methane loading. The impact associated with aerosols and the change in atmospheric composition is shown to be as large as the impact due to methane itself. A NO<sub>x</sub> mitigation strategy was evaluated by SOSAA as effective to remove methane but the side product of hazardous tropospheric ozone makes the method unfavourable in real life.

The process-based model SOSAA developed during this doctoral study is a useful tool for atmospheric research since it provides flexibility in time and space. The results call for further research into the ultimate mechanisms controlling nucleation and particle growth. This thesis also identifies knowledge gaps in the related precursor gases and encourages further studies in fields such as emission inventory of volatile organic compounds, sulphuric acid production, and atmospheric oxidation cycle.

Keywords: aerosol microphysics, chemistry, VOC, process based modelling, boundary layer

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## List of publications

This thesis consists of an introductory review, followed by five research articles. In the introductory part, the papers are cited according to their roman numerals. **Papers I, III, IV** and **V** are reproduced under the Creative Commons Licence. **Paper II** is reproduced with the permission granted by the Boreal Environment Research Publishing Board.

- I Boy, M., Sogachev, A., Lauros, J., Zhou, L., Guenther, A. and Smolander, S. (2011). SOSA – a new model to simulate the concentrations of organic vapours and sulphuric acid inside the ABL – Part 1: Model description and initial evaluation. *Atmos. Chem. and Phys.*, 11(1): 43-51.
- II Zhou, L., Nieminen, T., Mogensen, D., Smolander, S., Rusanen, A., Kulmala, M., and Boy, M. (2014). SOSAA – a new model to simulate the concentrations of organic vapours, sulphuric acid and aerosols inside the ABL – Part 2: Aerosol dynamics and one case study at a boreal forest site. *Boreal Environ. Res.*, 19 (suppl.B): 237-256.
- III Zhou, L., Gierens, R., Sogachev, A., Mogensen, D., Ortega, J., Smith, J. N., Harley, P. C., Prenni, A. J., Levin, E. J. T., Turnipseed, A., Rusanen, A., Smolander, S., Guenther, A. B., Kulmala, M., Karl, T. and Boy, M. (2015). Contribution from biogenic organic compounds to particle growth during the 2010 BEACHON-ROCS campaign in a Colorado temperate needleleaf forest. *Atmos. Chem. and Phys.*, 15: 8643-8656.
- IV Wang, Z. B., Hu, M., Mogensen, D., Yue, D. L., Zheng, J., Zhang, R. Y., Liu, Y., Yuan, B., Li, X., Shao, M., Zhou, L., Wu, Z. J., Wiedensohler, A. and Boy, M. (2013). The simulations of sulphuric acid concentration and new particle formation in an urban atmosphere in China. *Atmos. Chem. and Phys.*, 13(21): 11157-11167.
- V Kurtén, T., Zhou, L., Makkonen, R., Merikanto, J., Räisänen, P., Boy, M., Richards, N., Rap, A., Smolander, S., Sogachev, A., Guenther, A., Mann, G. W., Carslaw, K. and Kulmala, M. (2011). Large methane releases lead to strong aerosol forcing and reduced cloudiness. *Atmos. Chem. and Phys.*, 11(14): 6961-6969.

# 1 Introduction

This doctoral study is motivated by the profound impacts of aerosols on climate, air quality and human health. Aerosols may pose a serious threat to health when inhaled and deposited in the respiratory system (Nel, 2005; Reiss et al, 2007; Mauderly and Chow, 2008). As a common air pollutant, aerosols alter the concentration of important atmospheric oxidants and pollutants by offering surfaces for heterogeneous chemical reactions (Meilinger et al., 2001; Lou et al., 2014). Aerosols also degrade visibility due to their light scattering and absorbing ability (Hand et al., 2002; Lin et al., 2014). From a climate perspective, aerosols directly influence the radiative balance of the Earth through their optical properties (Myhre et al., 2013; Wang et al., 2013). Aerosols indirectly affect climate through cloud interactions, which have been the subject of intensive research in recent decades because the indirect effect remains the largest uncertainty in estimates and interpretations of the Earth's changing energy budget (Boucher et al., 2013).

Aerosols can be emitted directly to the atmosphere as primary particles, such as sea salt or dust, or they form in the atmosphere via gas-to-particle conversion as secondary particles. Such atmospheric secondary aerosol formation events, interchangeably referred to as new particle formation (NPF), have been observed around the world in various environments (Kulmala et al., 2004). It has been shown that NPF may increase cloud condensation nuclei (CCN) concentrations, especially on a regional scale (Merikanto et al., 2010; Kerminen et al., 2012). On a global scale, up to 50% of the CCN concentrations could originate from atmospheric NPF (Spracklen et al., 2008). This thesis is focused on NPF in the boundary layer in different environments, which is important in the atmospheric aerosol system and potentially has a large impact on air quality and climate.

The exact mechanisms behind atmospheric NPF have not yet been confirmed. Based on experimental evidence, Kulmala et al. (2013) have proposed that the initial formation of atmospheric particles as a two-step process. In the first step, atmospheric nucleation or the formation of stabilized clusters will occur in size range up to 2 nm. In the second step, the clusters are activated to grow over 3 nm by organic vapours. In the first step of nucleation, the importance of sulphuric acid has been confirmed by various studies (Lovejoy et al., 2004; Berndt et al., 2005; Sipilä et al., 2010). However, the atmospheric sulphuric acid concentration is too low to explain for the observed nucleation rates in the boundary layer (Kirkby et al., 2011). Compounds other than  $\text{H}_2\text{SO}_4$  have been proposed as being of equal or even greater importance for nucleation under certain conditions (Kerminen et al., 2010; Zhang et al., 2010; Almeida et al., 2013). For example, ions formed from the background atmospheric galactic cosmic rays have been suggested to be a potential important mechanism for nucleation (Curtius et al., 2007; Boy et al., 2008; Nieminen et al., 2011), but their contribution was later proved to be small in the boundary layer by chamber experiment CLOUD at CERN (Almeida et al., 2013). In coastal areas, iodine oxide has been suggested as nucleating vapour by both observations and model studies (O'Dowd and Hoffmann, 2005; O'Dowd and De Leeuw, 2007; Vuollekoski et al., 2009). In the laboratory, amines

were observed to significantly enhance nucleation. Sulphuric acid-amine nucleation proceeding via a base-acid stabilization mechanism is observed to be sufficient to account for particle formation rates observed in the atmosphere (Almeida et al., 2013). However, field observations have found both the presence and absence of an amine fraction in newly formed particles (Smith et al., 2010; Zhao et al., 2011; Creamean et al., 2011). The variation in observations suggests that amines may only explain a portion of atmospheric nucleation, mainly in the area where their emissions are high. The oxidation products of volatile organic compounds (VOCs) are also proposed to play a significant role in the initial steps of NPF due to their non-volatility or extremely low volatility (Zhang et al., 2004; Ehn et al., 2014; Schobesberger et al. 2013; Kokkola et al., 2014). In addition to their potential role in nucleation, organic compounds have dominant influence on particle growth. Organic compounds that are non-volatile or of extreme low volatility are crucial in the second step of initial formation of particles as they activate the growth of stabilized clusters (Kulmala et al. 2013; Ehn et al., 2014). The major contribution of organic compounds in particle growth to CCN sizes has also been confirmed by numerous observations worldwide (Held et al. 2004; Boy et al., 2005; Zhang et al., 2007; Jimenez et al., 2009; Yu et al., 2014).

We have quite substantial knowledge about the above mentioned precursor gases, including their sources, the general chemical reaction pathways, and their removal mechanisms, but knowledge gaps are evident too. For example, sulphuric acid is known to be produced mainly from the oxidation of sulphur dioxide ( $\text{SO}_2$ ) by hydroxide (OH) and lost through condensation to background particles (Eisele and Tanner, 1993; Weber et al., 1997). However, the calculated sulphuric acid concentrations based on our current knowledge are often lower than ambient measurements. Recent updates in  $\text{SO}_2$  oxidation by stabilized Criegee intermediates may provide an additional source of  $\text{H}_2\text{SO}_4$  in environments where VOCs are abundant (Boy et al., 2013). Although hundreds of biogenic volatile organic compounds (BVOCs) have been identified (Guenther et al., 2006), various biological and physical factors influencing the emissions of BVOCs introduce uncertainties in quantifying their emission rates (e.g. Schurgers et al., 2009; Han et al., 2013, Smolander et al., 2014). Once they have been emitted to the atmosphere, BVOCs undergo various oxidation processes (Lelieveld et al., 2008; Mogensen et al., 2015). The interaction between BVOCs and atmospheric oxidants has been a subject of active research due to the huge number of different species, many atmospheric chemistry reaction pathways and the potential influence on formation of secondary organic aerosols.

Apart from the complex relationship between precursor gases and particle formation mechanisms, airborne particles are constantly influenced by meteorological transport, turbulent mixing and deposition. For example, Nilsson et al. (2001) proposed that some NPF phenomena were initiated by the dilution of background particles due to entrainment and turbulent diffusion. Paris et al. (2009) suggested that the ultrafine particle concentration in the mid- and upper troposphere may be related to the lifting of boundary-layer air masses.

In summary, it is necessary to take into account all physical, chemical and meteorological processes when studying aerosol formation, their climate feedbacks, and their impacts on

air quality and human health. A chemical transport model with detailed chemistry and aerosol microphysics, SOSAA, has been constructed to address transport, emissions, chemistry and aerosol formation processes in this doctoral study. Several model studies were conducted in different environments and in a hypothetical methane-emission scenario. The aim is to further investigate atmospheric aerosols and their precursor gases in the boundary layer, where exchanges between the surface and the atmosphere take place. Specific objectives in this doctoral study include:

- Construct a one-dimensional chemical transport model with detailed chemistry and aerosol microphysics which is applicable for long term simulation (**Papers I and II**).
- Improve understanding of the major aerosol precursor gases (VOCs and H<sub>2</sub>SO<sub>4</sub>) and the main atmospheric oxidant OH by identifying possible reasons for discrepancies between simulations and observations. Special attention is paid to the estimation of VOC concentrations, the production of H<sub>2</sub>SO<sub>4</sub> and the budget of OH. (**Paper II to IV**).
- Evaluate particle nucleation mechanisms against field measurements in both clean continental and urban environments (**Paper II and IV**).
- Improve understanding of particle growth with a focus on the contribution from the oxidation products of BVOCs (**Paper II to IV**).
- Assess the climatic consequences of a hypothetical high methane release to the atmosphere. While similar assessment has been carried out earlier, we aim to improve the assessment by analysing the possible radiative effects from the methane-OH-aerosol link as well as evaluating a NO<sub>x</sub>-mitigation strategy to remove methane (**Paper V**).

## 2 Methods

The studies in this thesis combined process-based modelling and field observations. The observation data is not only used as input for model simulations, but is also utilized to assess the model performance and guide our analysis. Since the studies were conducted in different environments and multiple types of data were used, Section 2.1 presents the general characteristics of each site under investigation, and the main instruments from which the data were obtained. Sections 2.2, 2.3 and 2.4 present the employed model tools and parameterizations.

### 2.1 Field observations

#### 2.1.1 Rural continental site

The site of interest in **Paper I** and **II** is the Station to Measure Ecosystem-Atmosphere Relation (SMEAR II), a boreal forest site located in Hyytiälä, Finland (61°51'N, 24°15'E, 181 m a.s.l.). The vegetation at the site consists mainly of pine (>60%) and the rest are spruce, aspen and birch (Aaltonen et al., 2011). Due to the lack of emission studies other than pine trees, it is assumed in the model studies that the forest consists of 100% pine. It is a reasonable assumption when considering the area near the measurement station. During the modelling period, the canopy height is ~18.5 m with a canopy depth of ~9 m. The total leaf area index (LAI) is 5.8. The dominant emission at the site is monoterpenes, which is generally true for the European boreal zone (Hakola et al., 1998; Hauff et al., 1999; Rinne et al., 2007). The site is representative for clean continental environments although there are occasional anthropogenic air mass intrusions from the pellet factory and sawmills around 15km away and the city Tampere 60 km to the southwest. A detailed description of the SMEAR II station and the instrumentations at the site is given by Hari and Kulmala (2005) and at <http://www.atm.helsinki.fi/SMEAR/>.

#### 2.1.2 Mountainous site

The site studied in **Paper III** is the Manitou Experimental Forest Observatory (MEFO) located in the Front Range of the Colorado Rocky Mountains (39°6'N, 105°6'W, 2370 m a.s.l.). It is a mountainous site in close proximity to large urban centres (e.g. Denver is about 85 km to the northeast and Colorado Springs about 40 km to the southeast). Due to the shielding effect of the Rampart Range to the east and Pikes Peak to the south, the site normally encounters clean continental air masses from the southwest. Exceptions include episodic but frequent intrusions of anthropogenic air masses due to upslope flow during the morning and air moving downslope from the south during the evenings. Ponderosa pine is the main tree species at the site. Local emissions are dominated by 2-Methyl-3-Buten-2-Ol (MBO) and monoterpenes (Karl et al., 2014; Kaser et al., 2013a, b; Kim et al.,

2010). The median tree age at the site was 49.5 years and the average canopy height was 18.5 m in 2010 (DiGangi et al., 2011). Simulations were done for the BEACHON-Rocky Mountain Organic Carbon Study (BEACHON-ROCS) carried out at MEFO during August 2010. Ortega et al. (2014) have provided detailed description of MEFO site and BEACHON-ROCS campaign.

### 2.1.3 Urban site

The site studied in **Paper IV** is in Beijing, China, which is representative of a polluted urban environment. The sampling instruments are located on the sixth floor of an academic building on the campus of Peking University (39°59'N, 116°19'E). There are two major roads with heavy traffic 200 m away to the east and 500 m away to the south. The area is mostly residential. Detailed site descriptions can be found in Wu et al. (2008).

### 2.1.4 Major measurement instruments

All observation data of VOCs used in the studies were measured on sites with the Proton Transfer Reaction – Mass Spectrometer (PTR-MS) (Hansel et al., 1995; Lindinger et al., 1998; Lindinger and Jordan, 1998). It is an online instrument that measures atmospheric concentrations of various VOCs species continuously at a high frequency. The general instrumentation design is such that after VOCs are sucked into the system, they are first ionized by proton transfer from the ion source. The ion source is  $\text{H}_3\text{O}^+$ , which is produced by ionization of water vapour. Then the ionized VOCs molecules are guided via an electric field so that they are detected based on the mass-to-charge ratio. The general uncertainty of the PTR-MS measurements is estimated to be about 15% (Kaser et al., 2013a, Taipale et al., 2008). The detection limit varies from compound to compound. In the case of monoterpenes, the limit is around 0.01 ppbv (Taipale et al., 2008; Kaser et al., 2013b).

Sulphuric acid concentrations are measured using Chemical-Ionization Mass Spectrometry (CIMS) (Eisele and Tanner, 1993; Tanner et al., 1997). The methodology is similar to the PTR-MS. The main difference is the choice of ion source. The ion source used in CIMS instrument for measuring  $\text{H}_2\text{SO}_4$  is the  $\text{NO}_3 \cdot \text{HNO}_3$  ion, which only reacts with a few trace gas species in the atmosphere that are more acidic than  $\text{HNO}_3$ . Species less acidic than  $\text{HNO}_3$  will not be able to extract the proton. The uncertainty for  $\text{H}_2\text{SO}_4$  measurements with the CIMS is estimated to be 30% - 60% (Plass-Dülmer et al., 2011; Kim et al., 2013). The observations of OH used in all studies were also obtained from the CIMS. The measurement of OH with CIMS is not direct. The OH is titrated to  $\text{H}_2\text{SO}_4$  by letting it react with isotopically labelled  $\text{SO}_2$  and the concentration is extracted from the measurements of  $\text{H}_2\text{SO}_4$ . Eisele and Tanner (1991) have provided a detailed description of this method. The uncertainties for OH measurements are estimated to be ~35% with a detection limit at  $2 - 4 \times 10^5$  molecules  $\text{cm}^{-3}$  (Petäjä et al. 2009; Kim et al., 2013).

Particle number size distributions used for the studies in **Paper II** and **III** are measured at ground level using a differential mobility particle sizer (DMPS). The measured size range

in **Paper II** is from 3 nm to 1  $\mu\text{m}$  and in **Paper III** from 15 to 350 nm. The sampling flow first passes through a diffusion drier and a bipolar charge neutralizer. Then particles are size selected using a differential mobility analyser (DMA) and counted with a condensation particle counter (CPC). The particle number size distribution used in **Paper IV** is measured by a twin differential mobility particle sizer (TDMPS) consisting of two parallel DMA (Birmili et al., 1999). The measured size range is from 3 to 900 nm.

## 2.2 UHMA

The University of Helsinki Multicomponent Aerosol model (UHMA, Korhonen et al., 2004) was originally developed to study tropospheric new particle formation under clear sky conditions. It has basic aerosol microphysics including nucleation, condensation, coagulation and deposition. In the model, particles are assumed to be spherical and distributed in size bins based on the diameter. The UHMA model was modularized and implemented to the one-dimensional chemical transport model SOSAA (model to Simulate the concentration of Organic vapours, Sulphuric Acid and Aerosols) and the zero-dimensional version of MALTE (Model to predict new Aerosol formation in the Lower TropospherE, Boy et al., 2006). Deposition of particles in UHMA is ignored because this process is simulated by relevant schemes in SOSAA. Both SOSAA and MALTE provide necessary inputs for aerosol microphysics simulation, which include an initial particle number size distribution, ambient temperature, relative humidity and precursor gas concentrations. All studies in this thesis utilized the aerosol microphysics schemes originally from UHMA. Details about particle nucleation and growth parameterizations used in the studies in this thesis are presented below.

### 2.2.1 Nucleation

Since the exact mechanism driving nucleation remains unknown, three commonly used nucleation parameterizations (activation nucleation, kinetic nucleation and organic nucleation) were evaluated. The nucleated clusters are added to the first size bin defined in the model. In activation nucleation parameterization, the nucleation rate,  $J_{\text{act}}$ , is predicted to have a linear relationship with sulphuric acid concentration,  $[\text{H}_2\text{SO}_4]$ , such that:

$$J_{\text{act}} = K_{\text{act}} \cdot [\text{H}_2\text{SO}_4] \quad (1)$$

where  $K_{\text{act}}$  is the activation nucleation coefficient.

In the kinetic nucleation parameterization, two sulphuric acid molecules collide to form a cluster as in the kinetic gas theory. Some of the formed clusters will break apart while some will remain stable and grow further to particles. The nucleation rate,  $J_{\text{kin}}$ , is related to sulphuric acid concentration,  $[\text{H}_2\text{SO}_4]$ , as follows:

$$J_{\text{kin}} = K_{\text{kin}} \cdot [\text{H}_2\text{SO}_4]^2 \quad (2)$$

where  $K_{\text{kin}}$  is the kinetic nucleation coefficient that includes both the collision frequency and the probability of forming a stable cluster after the collision (Weber et al., 1997; Sihto et al., 2006; Lauros et al., 2011).

Metzger et al. (2010) presents an attempt in studying the influence of organic oxidation products on nucleation. Schobesberger et al. (2013) suggests that monoterpene oxidation products may cluster directly with a single sulphuric acid molecule based on both field observations and laboratory experiments. For this reason, particle nucleation is also studied in this thesis with an organic nucleation parameterization, in which the sum of first stable oxidation products from reactions between OH and monoterpenes ( $\alpha$ -pinene,  $\beta$ -pinene and limonene in **Paper II**;  $\alpha$ -pinene and  $\beta$ -pinene in **Paper IV**) were chosen to represent the organic compound (Org). The nucleation rate,  $J_{\text{org}}$ , is parameterized in the same way as in Metzger et al. (2010) as:

$$J_{\text{org}} = K_{\text{org}} \cdot [\text{H}_2\text{SO}_4] [\text{Org}] \quad (3)$$

where  $K_{\text{org}}$  is the organic nucleation coefficient.

Since the exact mechanisms driving atmospheric nucleation is not fully understood, the nucleation coefficient incorporates uncertainties due to unknowns as well as the potential effect of environmental variables such as temperature and humidity. The above three nucleation parameterizations have been applied in various studies and the nucleation coefficients have shown large variations across different sites (Paasonen et al., 2010). For this reason, a sensitivity test was performed to find the most suitable nucleation coefficient in each study. During the sensitivity test, both the total particle number concentrations and the time evolution of the number size distributions were compared between the simulations and observations.

### 2.2.2 Particle growth

UHMA has incorporated multicomponent condensation with a revised treatment of condensation flux onto free molecular regime particles (Lehtinen and Kulmala, 2003). Besides sulphuric acid, organic compounds were included in simulating the particle growth. Due to the variation in BVOCs emissions and the ambient organic trace gas spectrum in different environments, the exact organic condensation vapours used in each study are listed in Tables 1 and 2.

Table 1. Organic condensing vapour used for simulations at Hyytiälä and Beijing.

Boreal forest site, Hyytiälä ( <b>Paper II</b> )	Lumped sum of first stable reaction products from OH, O <sub>3</sub> , NO <sub>3</sub> oxidation of monoterpenes.
Urban site, Beijing ( <b>Paper IV</b> )	Lumped sum of first stable reaction products from OH, O <sub>3</sub> , and NO <sub>3</sub> oxidation of all organic compounds listed in Section 2.4.

Table 2. Three sets of organic condensing vapours tested in modelling experiments in study at the mountainous site, Manitou (**Paper III**).

Experiment I	Lumped sum of first stable reaction products from OH, O <sub>3</sub> , NO <sub>3</sub> oxidation of monoterpenes.
Experiment II	Lumped sum of first stable reaction products from OH, O <sub>3</sub> , NO <sub>3</sub> oxidation of MBO.
Experiment III	Lumped sum of first stable reaction products from OH, O <sub>3</sub> , NO <sub>3</sub> oxidation of monoterpenes, plus lumped sum of first stable reaction products from OH oxidation of MBO

### 2.3 SOSAA

SOSAA is a one-dimensional chemical-transport model with detailed aerosol microphysics. The last ‘A’ in the model name stands for ‘aerosol’, which makes the difference from the earlier model version SOSA which has no aerosol microphysics. The model column extends from the ground up to 3 km altitude, with flexibly defined horizontal height level. The model was constructed to study various processes in the planetary boundary layer in and above a forest canopy, including vertical transport, biogenic emissions, air chemistry and aerosol microphysics (**Papers I, II**, Smolander et al., 2014). These four processes have been modularized so that the model is optimized for implementing various parameterizations.

The meteorology module is based on the one-dimensional version of SCADIS (SCALAR DISTRIBUTION, Sogachev et al., 2002, 2012). It consists of prognostic equations for meteorological quantities including temperature, wind speed, humidity and heat fluxes. With the upper boundary conditions adjusted to synoptic-level temperature, wind and humidity, nudging is applied to force estimations of these variables toward observations. The emission module is based on either MEGAN (Model of Emissions of Gases and Aerosols from Nature, Guenther et al., 2006, 2012) or SIM-BIM (Seasonal Isoprenoid synthase Model – Biochemical Isoprenoid biosynthesis Model, Grote et al., 2006). In the chemistry module, chemical equations are mostly selected from the Master Chemical Mechanism, MCM v3.2 (Jenkin et al. 1997, Saunders et al., 2003, Jenkin et al., 2003; see <http://mcm.leeds.ac.uk/MCM>). The equations are translated to FORTRAN code by the Kinetic PreProcessor (KPP, Damian et al., 2002). There are slight differences in the compounds and equations included in each study based on the different emission at the sites. The exact chemistry scheme used in each study is described in the method description section of each manuscript. The aerosol microphysics module is based on the UHMA model described in Section 2.2.

The four modules are combined in a typical split-operator approach. Meteorology is simulated with a 10 s time step while the three other processes are simulated with 60 s time

step. After six meteorology time steps, emissions, chemistry and aerosols are each simulated over a 60 s time step. Model SOSAA is coded in FOTRAN with the MPI parallel libraries.

The required model inputs can be divided into four groups. The first group includes the land cover characteristics of the site being studied, such as leaf density, canopy height. The second group consists of meteorological parameters such as radiation conditions, vertical profiles of wind speed, temperature and humidity. ERA-Interim reanalysis data by ECMWF (Dee et al., 2011) were used as the boundary layer condition for wind speed, temperature and humidity at the upper border of the model column. The third group consists of measurements of five inorganic gas concentrations (NO, NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub> and CO) and calculated condensation sinks for sulphuric and nitric acids based on Pirjola et al. (1999). The last group of input data are the measured particle number size distributions. The model only reads in the measured number size distribution once a day at midnight for initialization.

## 2.4 MALTE

The study conducted at the urban site in China utilized the zero-dimensional version of MALTE (**Paper IV**). Detailed descriptions of MALTE are given by Boy et al. (2006, 2008) and Lauros et al. (2011). The zero-dimensional MALTE uses the chemistry module described in Section 2.3 and the aerosol microphysics module described in Section 2.2. The model can be seen as a scaled-down version of SOSAA as it does not account for vertical transport. In the study at urban China, the model function of simulating emissions was switched off. Instead, the model inputs include measured concentrations of organic vapours (methanol, acetaldehyde, acetone, isoprene, methyl ethyl ketone, methyl acrolein, methyl ethyl ketone, benzene, toluene, styrene, aromatic compounds including 8 and 9 carbon atoms respectively and monoterpenes). Other inputs include concentrations of the inorganic gases NO, NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub> and CO as well as ambient conditions such as temperature, humidity and radiation.

## 3 Results and discussions

### 3.1 Modelling transport process by SOSAA

This section aims to evaluate the ability of model SOSAA to reproduce transport in the boundary layer. The description of the turbulent boundary layer using a one-dimensional model necessarily requires simplifications of the real three-dimensional world. For this reason, the model SOSAA works best for horizontally homogeneous terrain. The terrain at the boreal forest site, Hyytiälä, is flat and the vegetation there is homogenous, which makes it a relative easy site for SOSAA to model boundary layer meteorology. At Hyytiälä, spring is the season with most frequent NPF event and summer is the season with highest biogenic emissions. For this reason, March and August 2006 were chosen for analysis in **Paper I**. Various meteorological parameters, including temperature, friction velocity, sensible and latent heat fluxes are modelled and compared to the measurements from Hyytiälä (**Paper I**). The results demonstrate that the model is able to reproduce measured meteorological variables with good agreement most of the time. Discrepancies are mainly due to the inability of the model to react to very fast changes of surrounding conditions such as the passage of atmospheric fronts. At nights with strong temperature gradients, the model tends to underestimate temperature decreases. The model also tends to overestimate the negative sensible heat flux during the night, which is possibly due to cloudiness which is currently not included in the model. In summary, the model is suitable for our purposes in reconstructing the vertical transport of precursor gases and aerosols at Hyytiälä.

In contrast, the mountainous site, Manitou, has highly variable meteorological condition that is challenging for modelling the transport. The site is under the influence of diurnal mountain-valley flows, meaning that the diurnal temperature variation is large. The model simulates comparable temperatures and humidities during the daytime but overestimates the two quantities at night. The wind speed is well-modelled during the day but is underestimated during the night. These discrepancies are due to the mentioned drainage flow related to the mountainous topography, which a column model cannot capture. The modelled latent heat flux is generally comparable with observations except during the morning when the model underestimates fluxes slightly. In general the sensible heat flux is overestimated during daytime, possibly due to the inaccuracies in prescribing soil heat fluxes and net radiation. The friction velocity is well simulated during the day but underestimated during the night, which may also be related to the nighttime drainage flow. Boundary layer evolution is assessed with sounding measurements during the BEACHON-ROCS campaign. The nighttime boundary layer height at this site can sometimes be as low as 40 m. In summary, the model SOSAA is satisfactory in reproducing the meteorology for the mountainous environment during the daytime. Nighttime simulation is less reliable due to the drainage flows down the mountain. Therefore the Manitou analysis for chemistry and aerosols is focused on the daytime conditions.

## 3.2 Aerosol precursor gases

### 3.2.1 Biogenic volatile organic compounds

Monoterpenes are the main BVOCs modelled at the boreal forest site in Hyytiälä (HYY), Finland for March to August 2010 and at the mountainous forest site in Manitou (MEFO), USA, for August 2010 (**Papers II and III**). At both sites, the concentrations of monoterpenes exhibit a clear diurnal variation such that the concentrations are high during the night and low during the day (Fig. 1). The nighttime concentration is high mainly due to the suppressed boundary layer height and decreased losses from oxidation. On the other hand, the concentration decreases during the daytime as the boundary layer height and concentration of OH increase. The observed monoterpene concentrations at both sites are at a similar level, although the variation in concentration levels is more significant at Manitou than at Hyytiälä. As well as the different forest emissions of monoterpenes at the sites which may explain for some of the variations, the low nighttime boundary layer height in Manitou may also cause the high concentrations of monoterpenes observed below the canopy. Figure 1 shows that SOSAA simulates the monoterpene concentration well compared to measurements at Hyytiälä for summer 2010. The model was then applied to provide monoterpene concentration at Hyytiälä for spring 2010 when measurements were not available. The simulation shows an increasing trend in monoterpene concentrations from spring to summer, which is expected as the emissions should be more active in the summer when there is more sunlight (see Fig. 2 in **Paper II**). Compared to Hyytiälä, the model

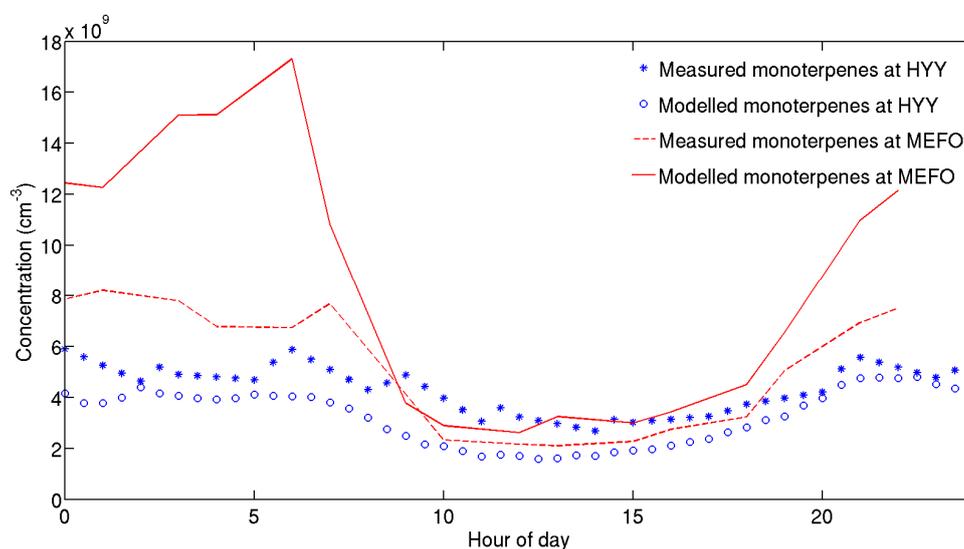


Figure 1: Averaged diurnal variation of the measured and modelled monoterpene concentrations at Hyytiälä (HYY) and Manitou (MEFO). The averages are calculated for Hyytiälä summer 2010 and for Manitou August 2010. Error bars have been omitted here for clarity. Error bars for the data from Hyytiälä could be found in Fig. 1 in **Paper II**, error bars for the data from Manitou could be found in the right panel of Fig. 4 in **Paper III**.

performance is less satisfactory at Manitou. The simulation for daytime concentration is good but it significantly overestimates the concentration at night. The main cause could be that the model overestimates the nighttime temperature by up to five degrees, which possibly leads to an overestimation of monoterpene emissions. Sensitivity studies have been conducted for the response of total monoterpene emission rates to temperature. An increase of five degrees Celsius at night may increase emission rates by 80% to 100%.

Unlike Hyytiälä where monoterpenes dominant the local biogenic emissions, at Manitou emissions are dominated by MBO. Both laboratory and field studies have suggested a possible contribution from MBO to secondary organic aerosol formation (Zhang et al., 2012 and 2014). For this reason, MBO is also studied as a precursor gas for aerosols at Manitou. In contrast to monoterpene concentrations, the concentration of MBO shows a diurnal variation that is high during the day and low during the night due to the light-driven property of MBO emission (Fig. 2). The daytime concentration of MBO is about two to four times that of monoterpenes. The simulation results indicate that SOSAA captures both the magnitude and variation of MBO concentration reasonably well.

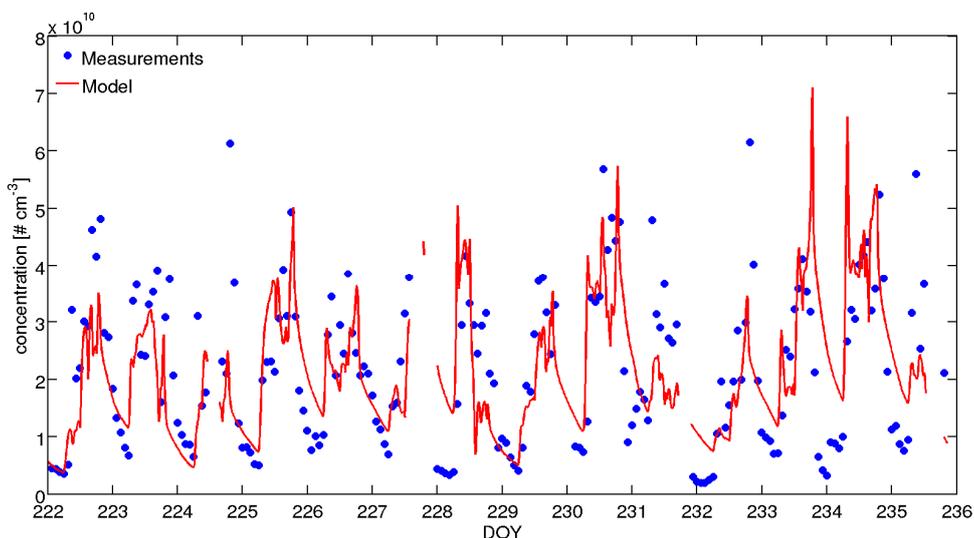


Figure 2: Measured and modelled MBO concentrations at 3.5 m above ground at site Manitou from 10 to 23 August 2010 (DOY 222 to 235). This figure is found in **Paper III** as Fig. 5.

### 3.2.2 Hydroxide

As one of the most important oxidants in the atmosphere, the concentration of hydroxide (OH) is studied at both Hyytiälä and Manitou. It can be seen that the OH level at Manitou is twice that at Hyytiälä (Fig. 3). This could be due to a higher photolysis production rate of OH at Manitou where the solar radiation is more intense than at Hyytiälä. It may also relate to the higher NO level at Manitou (about  $1.3 \times 10^{10}$  molecules  $\text{cm}^{-3}$ , Nakashima et al., 2014) compared to the level at Hyytiälä (about  $3.5 \times 10^9$  molecules  $\text{cm}^{-3}$ , Mogensen et al., 2011). Kim et al. (2013) pointed out, based on the observations at Manitou, that the recycling production of OH from ( $\text{HO}_2 + \text{NO}$ ) is  $\sim 20$  times higher than the photolysis

production of OH from ozone. The difference in OH level between the two sites is captured by the model, although the model simulations exhibit a degree of overestimation at both sites. The overestimation is expected because it is known that some OH reactivity is missing, meaning some sink terms of OH are missed (Di Carlo et al., 2004; Mogensen et al., 2011, 2015). The missing OH reactivity arises from compounds that react with OH in the atmosphere that we currently do not know or cannot measure. The overestimation of OH concentration at midday by  $\sim 80\%$  is reasonable when one considers the suggested missing OH reactivity of  $\sim 65\%$  at Hyytiälä (Mogensen et al., 2011 and 2015). Mogensen et al. (2011) pointed out that the main emitted biogenic compounds, monoterpenes, could only account for  $\sim 10\%$  of the total OH reactivity, and the large missing reactivity should mainly originate from uncounted hydrocarbons instead of inorganic compounds. Compared to Hyytiälä, the simulated OH concentration at Manitou is in better agreement with the CIMS instrument. Taking into account the 35% instrumental uncertainty, the results agree fairly well. At Manitou, the missing OH reactivity is only around 30%, which is thought to be due to some oxidation products of biogenic species (Nakashima et al., 2014). By estimating the main local emissions, MBO and monoterpenes, which should account for  $\sim 40\%$  of the total OH reactivity, SOSAA does a good job in reproducing OH concentration at Manitou.

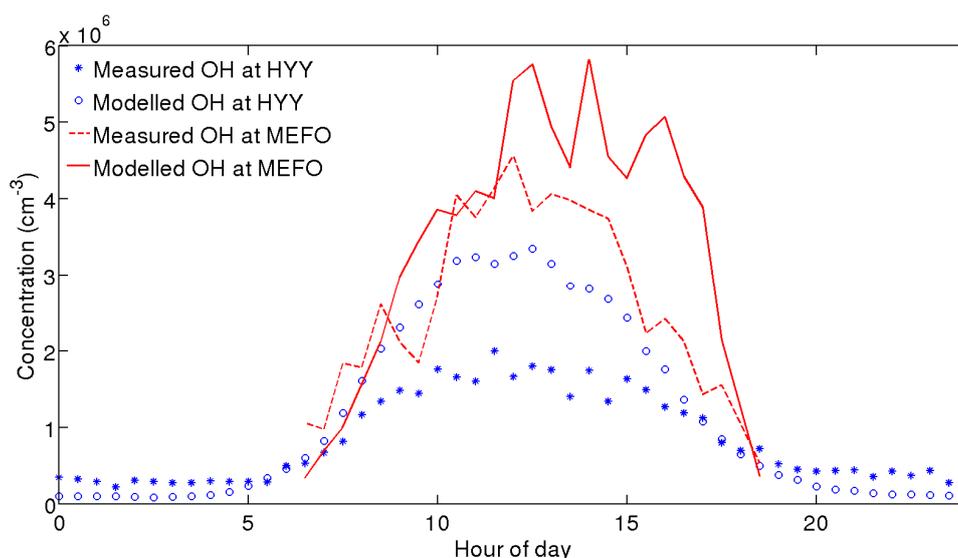


Figure 3: Averaged diurnal variation of the measured and modelled OH concentrations at Hyytiälä (HYY) and Manitou (MEFO). The averages are calculated for Hyytiälä summer 2010 and for Manitou August 2010. Error bars have been omitted here for clarity. Error bars for the data from Hyytiälä could be found in Fig. 3 in **Paper II**, error bars for the data from Manitou could be found in the left panel of Fig. 6 in **Paper III**.

### 3.2.3 Sulphuric acid

Despite including the latest updated reaction rates related to Criegee Intermediates from alpha-, beta-pinene and limonene, sulphuric acid concentrations are still underestimated at

both Hyytiälä and Manitou (Fig. 4). Taking into account the 35% uncertainty in  $\text{H}_2\text{SO}_4$  measurements at Manitou (Kim et al., 2013), the underestimation of  $\text{H}_2\text{SO}_4$  is still significant. The underestimation is less severe at Hyytiälä than at Manitou; however, the improvement is mainly due to the overestimated OH. If the condensing sink of sulphuric acid onto aerosols is not overestimated, then our results at both sites suggest that sources other than the oxidation of  $\text{SO}_2$  by OH are missing. The underestimation of  $\text{H}_2\text{SO}_4$  at night also hints at a source that is not related to photochemistry. The  $\text{H}_2\text{SO}_4$  level at Hyytiälä and Manitou are quite different. Although peak of  $\text{SO}_2$  concentrations of up to  $1 \times 10^{10}$  molecules  $\text{cm}^{-3}$  is observed at Manitou due to anthropogenic air mass intrusion, the average  $\text{SO}_2$  levels are similar between two sites, both in the range between 4 to  $5 \times 10^{10}$  molecules  $\text{cm}^{-3}$ . Based on this analysis, the difference in  $\text{H}_2\text{SO}_4$  level should mainly result from the difference in OH levels, because the OH oxidation of  $\text{SO}_2$  is the main production channel of  $\text{H}_2\text{SO}_4$  in atmosphere.

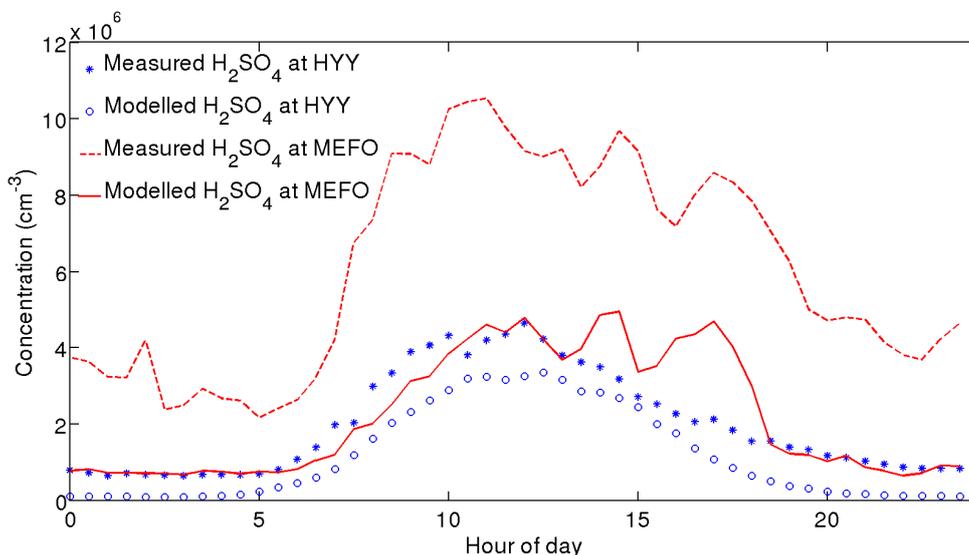


Figure 4: Averaged diurnal variation of the measured and modelled  $\text{H}_2\text{SO}_4$  concentrations at Hyytiälä (HYY) and Manitou (MEFO). The averages are calculated for Hyytiälä summer 2010 and for Manitou August 2010. Error bars have been omitted here for clarity. Error bars for the data from Hyytiälä could be found in Fig. 4 in **Paper II**, error bars for the data from Manitou could be found in the right panel of Fig. 6 in **Paper III**.

The two rural sites described above have shown differences with respect to the main VOCs, OH and  $\text{H}_2\text{SO}_4$  concentrations. The differences are mainly due to the different geographic locations and forest environments. The description of the precursor gases and related atmospheric chemistry is even more different when moving to an urban environment, where human activities are exerting strong influences. Compared to the studies at Hyytiälä and Manitou, limited observations were conducted in Beijing. By taking VOCs concentrations measured from the PTR-MS and measured inorganic gases as inputs (list of input gas concentrations is presented in Sec. 2.4), the  $\text{H}_2\text{SO}_4$  is modelled using the zero-dimensional version of MALTE model (**Paper IV**). Figure 5 shows that  $\text{H}_2\text{SO}_4$  is also underestimated in Beijing, by 10% to 40%, though it should be noted that CIMS instru-

ment has an uncertainty of 30% - 60% (Plass-Dülmer et al., 2011). The situation is different from Hyytiälä and Manitou in that the underestimation of  $\text{H}_2\text{SO}_4$  is likely due to an underestimation of the OH concentration. One significant source of OH is nitrous acid (HONO) (Su et al., 2008). The HONO production of OH is especially prominent during the morning when traffic is heavy, because traffic is the major emission source of HONO in an urban atmosphere (Kurtenbach et al., 2001). However, this source was not included in the model simulations. The limited measurement of HONO during the study period is not sufficient to be an input to the model, but it reveals that the modelled HONO concentration may be substantially underestimated by up to 90% during the rush hours from 6am to 12pm. Using measured HONO concentration as an input to the model for just the days when measurements are available, the sulphuric acid concentration increases by 1.5 – 2.5 times at its peak around 8am. The observed maximum midday sulphuric acid concentration varies between  $3.1 \times 10^6$  and  $1.1 \times 10^7 \text{ cm}^{-3}$ , which is comparable to the level at Hyytiälä

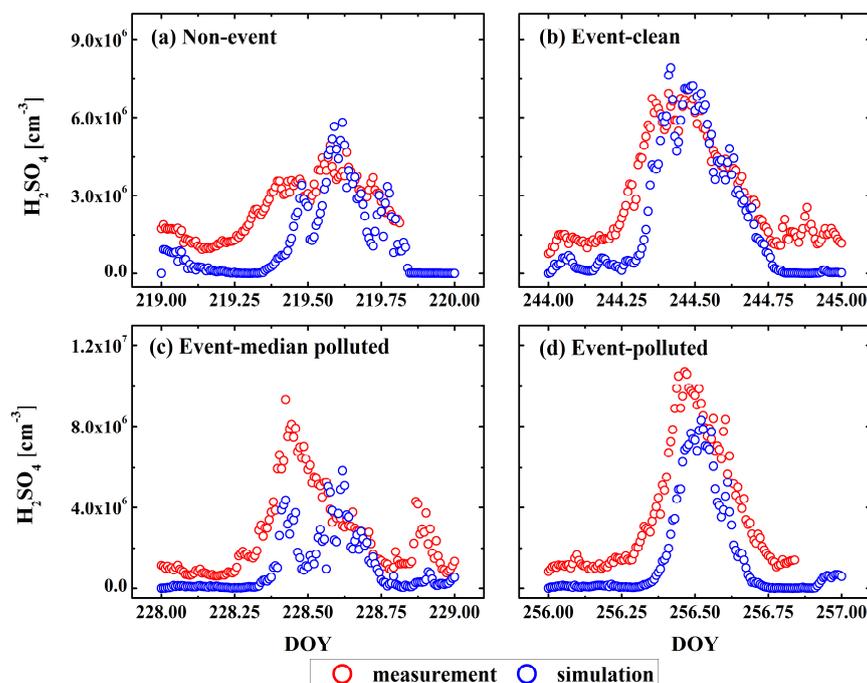


Figure 5: Measured (red) and modelled (blue) sulphuric acid concentrations for four selected days in diverse pollution conditions. (a) non-event day, (b,c,d) NPF event day. The x axis is presented by DOY (day of year). This figure is found in **Paper IV** as Fig. 1.

### 3.3 Aerosol formation

With the relevant precursor gases quantified at each site, model simulations were carried out to further study the atmospheric new particle formation events, which could be divided in to two steps: nucleation and growth of particles.

### 3.3.1 Nucleation

The commonly used nucleation parameterizations (activation nucleation, kinetic nucleation and organic nucleation) were described in Section 2.1.1 and evaluated at both the clean forest site, Hyytiälä, and the polluted urban site, Beijing (**Paper II and IV**). At both sites, observations of particle number size distribution on each day are classified according to Dal Maso et al. (2005) as event, non-event and undefined day. The appearance of a distinctive new mode of particles in the nucleation mode (particle diameter between 3 and 25 nm) and its subsequent growth in the following hours are the two requirements that must be satisfied when classifying a day as an event day. Satisfying one of the requirements classifies the day as an undefined day. 35 event days were observed at Hyytiälä from March to August 2010. The simulation with the kinetic nucleation parameterization captures all observed event days while the simulation with the organic nucleation parameterization misses one event day. In order to study the modelled behaviour of new particle formation events, “good days” are picked out when both the measurements and simulation indicate an event and particles grow to similar sizes; or when both the measurements and simulation indicate a non-event. With respect to the selected good days, both kinetic and organic nucleation parameterizations satisfactorily predict concentrations of nucleation mode particles (see Fig. 6). The correlation coefficient between simulations and observations during good days is slightly better in the case of kinetic (0.71) than for organic (0.65) nucleation simulations. In both cases, the simulated nucleation-mode (3-25 nm in diameter) particles show a similar trend to the sulphuric acid, so that overestimation is seen during the day while underestimation is seen during the night. In Hyytiälä study, the total particle concentrations (3 nm to 1 µm in diameter) have also been compared between simulations and DMPS measurements during sensitivity test of the nucleation coefficient. A single organic nucleation coefficient that gives comparable total particle concentration to the measurements during both spring and summer cannot be found. The organic nucleation parameterization that well predicts the total particle concentration in spring overestimates the concentration in summer. This result is not to say that the organic nucleation parameterization is wrong. Rather the selected organic nucleation compounds (OH oxidation products of major monoterpenes at the site) may not be a suitable proxy for predicting NPF events at Hyytiälä.

The Activation and kinetic nucleation parameterizations were evaluated at the urban site, Beijing, using the zero-dimensional model MALTE. The simulation using activation nucleation parameterization fails to capture the observed sharp increase in concentration of freshly nucleated particles between 3 and 6 nm during an event day. Compared to activation nucleation, the kinetic nucleation parameterization is better at predicting the freshly nucleated particles on both event and non-event days (see Fig. 3 in **Paper IV**). When comparing observed freshly nucleated particle (3 – 6 nm) concentrations at Hyytiälä and Beijing, the peak concentration of  $\sim 3000$  particles  $\text{cm}^{-3}$  at Beijing during an NPF event is on average up to two times higher than at Hyytiälä (Fig. 7). With similar level of sulphuric

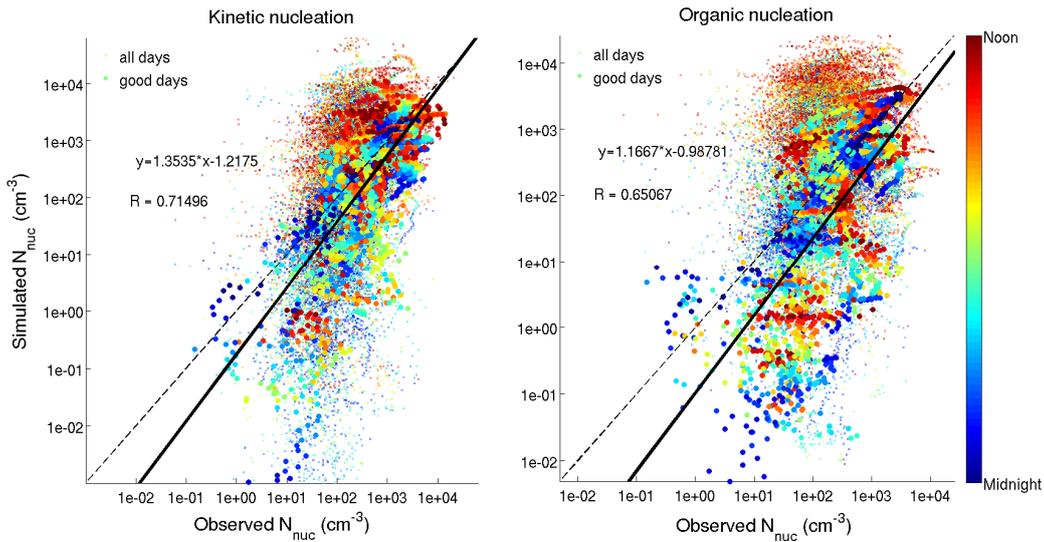


Figure 6: Modelled (y-axis) vs. measured (x-axis) number concentrations of nucleation mode (3-25 nm) particles,  $N_{\text{nuc}}$ , at Hyytiälä spring and summer 2010. Data points for the “good” days are dots while other data points are crosses. All points are coloured according to the time of day. The colour of data points is close to dark red if the time is close to noon and the colour is close to dark blue when the time is close to midnight. Data points at 6am and 6pm is coloured as green. The solid line is the regression fit for data points during “good” days and the dashed line represent one-to-one relation between simulation and observation. The left-hand plot is based on a simulation which uses the kinetic nucleation parameterization, and the right-hand plot is based on a simulation which uses the organic nucleation mechanism. The figure can be found in **Paper II** as Fig. 11.

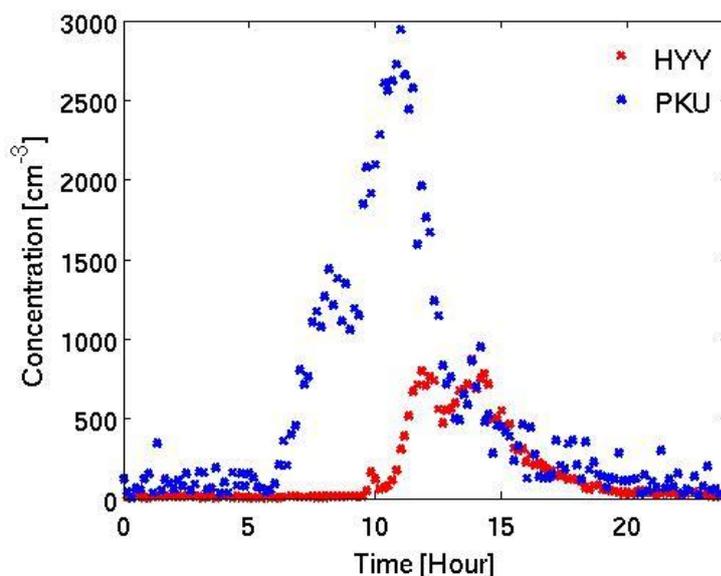


Figure 7: Averaged diurnal variation of the measured concentrations of particles between 3 and 6 nm at Hyytiälä (HYY) and Beijing (PKU). The average are calculated for 12 event days observed at Hyytiälä in March 2010 and 8 event days observed at Beijing in August and September 2008.

acid concentration (concentration peaks at  $3 - 10 \times 10^6$  molecules  $\text{cm}^{-3}$ ), the kinetic nucleation coefficient used for Beijing simulation is ten times the coefficient used for Hyytiälä. The large variation in nucleation coefficient suggests that the kinetic nucleation parameterization has a large uncertainty when predicting NPF. Besides the difference in magnitude, the peak number concentration at Beijing shown in Fig. 7 is also a few hours earlier than at Hyytiälä. The measurement site at Beijing is close to two main roads. It is observed that the freshly nucleated particle concentration starts to rise at about the same time as rush hour starts in the morning. It therefore seems likely that compounds originating from the traffic contribute to the observed nucleation at that site.

Besides activation and kinetic nucleation, the organic nucleation parameterization with oxidation products of monoterpenes was also evaluated at Beijing. It was demonstrated that organic nucleation simulation reproduces the observed NPF events satisfactorily, but the simulated peaks of freshly nucleated particle concentration show a clear delay of about two hours (see Fig. 6 in **Paper IV**). The message here is that the chosen oxidation products of monoterpenes by OH are not a good proxy for nucleation at this site. Improving model inputs and chemistry schemes related to organic compounds of anthropogenic origin, especially from traffic, should be able to improve results.

### 3.3.2 Particle growth

The main focus of the particle growth study is to assess the contribution from the oxidation products of volatile organic compounds (**Paper II to IV**). The first stable oxidation products of monoterpenes, which are the dominant BVOCs emissions at Hyytiälä, are shown to explain observed growth rates reasonably well (see Fig. 10 in **Paper II**). However, the monoterpene oxidation products are indicated by model simulations to be insufficient in growing the particles over the instrument's detection limit of 15 nm (Fig. 8, plot DMPS and Experiment I; Table 2 in Section 2.2.2, Experiment I). If only including the oxidation products of MBO (Table 2 in Section 2.2.2, Experiment II), the simulated particles can grow sufficient large to compare with the measurements, however, the model cannot simulate the continuing growth in the evening (Figure 8, plot DMPS and Experiment II). By combining the oxidation products of monoterpenes and MBO, Experiment III depicts a possible picture of how local biogenic emissions may contribute to observed particle growth at Manitou (Fig. 8, plot DMPS and Experiment III; Table 2 in Section 2.2.2, Experiment III). At Manitou, where the dominant BVOCs emission is MBO, the organic condensing compounds contributing to particle growth should have a similar daily pattern and concentration level to the sum of OH oxidation products of MBO. The high concentration of these compounds during the day can explain the observed fast initial growth of particles. However, MBO oxidation products alone could not reproduce the observed evolution of particle number size distribution due to the low level of MBO at night. The existence of  $\text{NO}_3$  oxidation products of monoterpenes are therefore suggested as an explanation of the continued growth of particles at night.

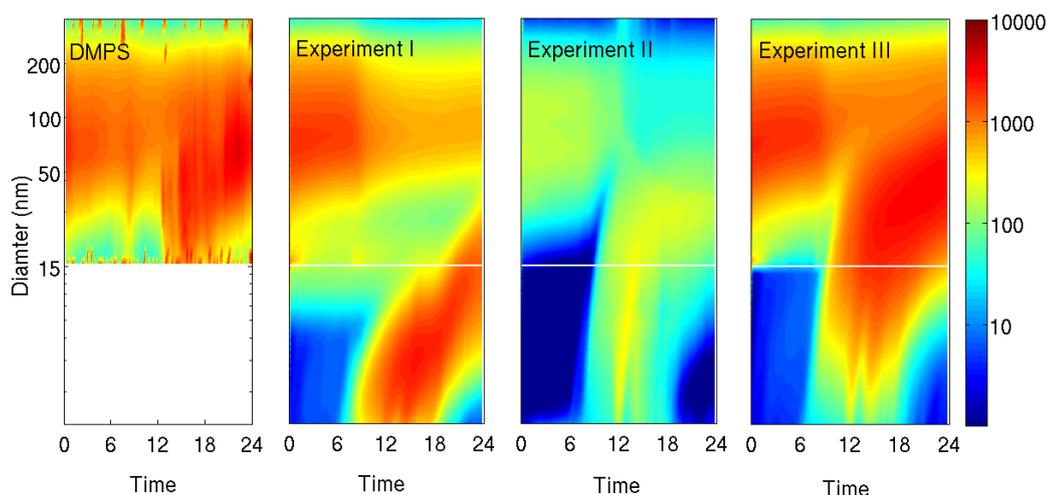


Figure 8: Averaged daily number size distributions based on the DMPS measurements and model Experiments I-III as explained in Sec. 2.2.2. The concentration unit is molecules  $\text{cm}^{-3}$ . The DMPS instrument has a cut-off size at 15nm. The averages are made only for periods when measurements are available. The figure can be found in **Paper III** as Fig. 9.

At the urban site, Beijing, BVOCs only contribute a fraction of the total VOCs budget. In order to include both biogenic and anthropogenic contributions, the organic condensing compounds are defined as the known first stable oxidation products from reactions between OH, O<sub>3</sub>, NO<sub>3</sub> and all included organic compounds. The simulation confirms the limited contribution of sulphuric acid to particle growth (Boy et al., 2003, Kuang et al., 2010). Composition analysis based on the model results also suggests that the dominant contribution to the volume of particles between 3 and 25 nm is from O<sub>3</sub> oxidation products ( $94.5\% \pm 2.6\%$  of volume), while the contribution from OH oxidation products is minor ( $5.5\% \pm 2.3\%$  of volume).

### 3.4 Climate impact of methane - OH - aerosol link

As well as its applications in detailed studies of precursor gas and aerosol formation in the real world, the model SOSAA was also applied in a hypothetical study to investigate the viability of perturbing tropospheric chemistry artificially to remove methane (**Paper V**). Methane (CH<sub>4</sub>) has a long atmospheric life time of about twelve years, and is suggested to have a greater warming potential than carbon dioxide (IPCC, 2007). Observations of large methane emissions in Arctic areas have heated up the discussion in media on the “clathrate gun” hypothesis, the rising temperature leads to the destabilization and subsequent release of methane clathrates in the Arctic permafrost and seabed into the atmosphere, which would in turn amplify the initial warming (Kennett et al., 2000).

**Paper V** first investigates the possible changes in methane lifetime, atmospheric OH level, cloud droplet number concentration (CDNC), and the consequent radiative effects in hy-

pothetic scenarios where methane concentration increased by factors of 10 and 100. A large increase in the methane concentration would increase the concentration of tropospheric ozone and stratospheric water vapour, while significantly decreasing tropospheric OH concentrations (Schmidt and Shindell, 2003; Shindell et al., 2009). Chemical transport model TOMCAT (Chipperfield, 2006) simulations indicate that in scenarios with 10 and 100 times current concentration of methane, the average tropospheric OH concentration decreases by about 47% and 79%. Since OH oxidation is the main sink of atmospheric methane, the lifetime of methane increases by between 70% and 233%. So in addition to the increased amount of methane, the increased lifetime of methane will also generate positive radiative effects. Furthermore, the decreased OH concentration is expected to reduce the formation rate of nucleating and condensing vapours, leading to a lower aerosol concentration and CDNC. This will lower the average cloud albedo, decrease cloud lifetimes and cloudiness, and thus further warm the climate. Both global models, GLOMAP (Mann et al., 2010) and ECHAM5-HAM (Stier et al., 2005) simulate a decrease in CDNC of 18% in the  $10 \times \text{CH}_4$  scenario and 35% in the  $100 \times \text{CH}_4$  scenario. A set of model simulations were done to assess the radiative forcings due to the three described aspects of radiative forcing (Table 3). The assessment shows that the total radiative forcing associated with a large methane increase may be around twice as large as the direct greenhouse enhancement of the added methane.

When assessing the possible mitigation strategy of increasing atmospheric  $\text{NO}_x$  levels to remove the methane, SOSAA suggests that in a  $10 \times \text{CH}_4$  scenario, a doubling of  $\text{NO}_x$  level would reduce the methane life time significantly by 40%. However, the global model TOMCAT simulation for the same scenario indicates only a modest reduction in methane lifetime of 9%. The discrepancy between the one-dimensional model SOSAA and the global model is likely related to the more detailed chemistry scheme included in SOSAA. However, other factors like the different emission scenarios for organic vapours and the selected assumption of cloud-free conditions in SOSAA could also be important. Despite of the large uncertainties associated with the results, however, the production of hazardous tropospheric ozone means that this method is unfavourable in real life.

Table 3. Various radiative forcing components estimates (calculated with the respect to the present-day atmosphere) in 10 times present-day  $\text{CH}_4$  level scenario ( $10 \times \text{CH}_4$ ) and 100 times present-day  $\text{CH}_4$  level scenarios ( $100 \times \text{CH}_4$ ).

	$10 \times \text{CH}_4$ (unit: $\text{W m}^{-2}$ )	$100 \times \text{CH}_4$ (unit: $\text{W m}^{-2}$ )
Forcing due to methane	2.51	6.56
Forcing due to ozone	0.76	1.13
Total aerosol forcing	2.32	5.54
Total forcing	5.59	13.23

## 4 Review of papers and the author's contribution

**Paper I** is the first model description paper for the model SOSA (the name changed to SOSAA in other manuscripts when aerosol microphysics module was implemented). It presents an attempt to reconstruct the emissions, transport and chemistry in the atmospheric boundary layer at a boreal forest site, Hyytiälä, Finland with SOSA. Simulated meteorological parameters such as the eddy diffusivity have been shown to agree well with the observations. Vertical profile of monoterpenes was simulated and it was found to have similar trend as the observed vertical profile of particle concentration. I contributed to the sensitivity analysis of model parameters (time steps in different module, number of column layers, nudging coefficients, etc.) and writing the manuscript.

**Paper II** is the second model description paper for the model SOSAA and it reports the results from the model's first study of aerosol formation. The concentration of major emitted biogenic organic compound, monoterpenes, is well simulated with emission module based on MEGAN. The concentration of OH is overestimated due to missing OH reactivity. The concentration of sulphuric acid is underestimated even with the latest Criegee intermediates reaction rates. Nucleation process is studied using kinetic and organic nucleation parameterizations. All event days were reproduced. The results indicate a similar performance by the two parameterizations with respect to the estimation of nucleation mode particle concentrations, though the organic nucleation parameterization overestimates the total particle concentration during the summer. I implemented the aerosol microphysics module in SOSAA. I did all of the simulations and major part of the data analysis, and I wrote the manuscript.

**Paper III** studies the growth of particles at Manitou and attempts to reconstruct the vertical transport and air chemistry at a mountainous site. Model SOSAA is shown to be able to simulate in situ meteorological conditions during the daytime. The concentrations of monoterpenes and MBO are well simulated during daytime. Nighttime concentration of monoterpenes is overestimated due to overestimated temperature. The simulated concentration of OH is comparable with the measurements. The implemented chemistry scheme with the latest Criegee intermediate reaction rates still underestimates the sulphuric acid concentration by 50%, indicating a missing source of atmospheric sulphuric acid. The aerosol simulations indicate that the main compounds condensing onto particles may have a similar concentration level and diurnal variation to the OH oxidation products of MBO, which is the dominant BVOCs emission at the site. The results also emphasize the importance of the low volatility of organic condensing compounds. I prepared all model inputs, did all of the model simulations and major part of the data analysis. I wrote most of the manuscript.

**Paper IV** investigates the sulphuric acid concentration and new particle formation in an urban environment in China, using the zero-dimensional version of MALTE model. The study reveals that an underestimated sulphuric acid concentration during morning rush hour may result from missing OH production, possibly due to the underestimated HONO from traffic emissions. The new particle formation events are well-captured by the kinetic and organic nucleation parameterizations. However, the organic nucleation parameterization predicts a delayed concentration peak for particles between 3 and 6 nm in diameter, possibly due to organic compounds from traffic emissions which are not fully accounted for in the model. Composition analysis based on simulation results suggests that the aerosol volume mainly consists of ozone oxidation products. I contributed to model development related to aerosol microphysics and writing the manuscript.

**Paper V** investigates the impacts of strongly elevated atmospheric methane level on atmospheric oxidant concentrations and the consequent radiative forcing changes based on multiple models. A 10-fold increase in methane concentrations is estimated to decrease OH concentrations and moderately increase ozone concentration, which further leads to a 70% increase in methane lifetime. The decrease in cloud condensation nuclei due to the methane-OH-aerosol link leads to further warming. The impact associated with aerosols and the change in atmospheric composition is shown to be as large as the impact due to the longwave radiative forcing of the elevated methane level. Model SOSAA was applied to assess the feasibility of the mitigation method of adding NO<sub>x</sub> to remove methane. The SOSAA simulation indicates that, in a scenario where the methane concentration is 10 times the present level, the methane lifetime could be significantly reduced by up to 40% if the NO<sub>x</sub> level is doubled. However, the negative side effect of hazardous tropospheric ozone production makes the strategy unfavourable in real life. I did radiative effects calculations for methane, SOSAA simulations and part of the results analysis. I also contributed to manuscript writing.

## 5 Conclusions

Understanding the effects and interactions between various atmospheric processes in the boundary layer is crucial for predicting the concentration of aerosols and CCN-sized particles, which will further enable us to predict the related air quality and climatic impacts. By properly describing the transport, biogenic emissions, atmospheric chemistry and aerosol microphysics, this thesis presents an attempt in reconstructing the chemical cycle of aerosol precursor gases and new particle formation in boundary layer via a modelling approach. Uncertainties of the developed model SOSAA and possible reasons for discrepancies between simulations and observations are identified. Outcome of this doctoral study will be discussed below by addressing each objective point listed in Section 1.

- A one-dimensional model, SOSAA, was constructed for boundary layer simulations with detailed chemistry and aerosol microphysics. Parallelization was implemented to model code which significantly reduces the computing time for simulations of long period. Detailed aerosol microphysics model, UHMA, was implemented to SOSAA. In addition, the aerosol microphysics in the zero-dimensional version of model MALTE was also updated with UHMA aerosol microphysics. The ability of SOSAA in reconstructing vertical transport has been tested as reliable for homogeneous terrain and for the daytime at mountainous terrain. (**Paper I to III**)
- The concentrations of main emitted BVOCs at two continental rural sites, Hyytiälä and Manitou, can be well estimated with model SOSAA. OH concentration is overestimated during daytime at both rural sites due to the missing OH reactivity. Despite of the overestimation in OH and the inclusion of updated reaction rates of Criegee intermediates, sulphuric acid concentrations are still underestimated, suggesting for missing source terms of sulphuric acid. At the urban site Beijing, OH concentration is likely underestimated due to the fact that HONO from traffic emissions is uncounted in the model. The possible underestimation in OH at Beijing thus explains for the underestimated sulphuric acid concentration, which is most prominent during morning rush hours. (**Paper II to IV**)
- Different nucleation parameterizations were evaluated at the clean continental site Hyytiälä and at the polluted urban site Beijing. The results suggest that kinetic nucleation parameterization is able to estimate the observed nucleation process and particle concentrations, but the uncertainty is large. Organic nucleation parameterization with OH oxidation products from monoterpenes are applied in search for possible nucleating compounds other than sulphuric acid. However, the results are not satisfying. At Hyytiälä, organic nucleation overestimates the total particle concentration during the summer when the monoterpenes emission is the highest. At Beijing, the organic nucleation shows a clear lag of about two hours in the peak concentration of particles between 3 and 6 nm. (**Papers II and IV**)
- Oxidation products of monoterpenes could well explain for the observed particle growth at Hyytiälä, where monoterpenes dominant the local BVOCs emissions. How-

ever, same oxidation products from monoterpenes are not sufficient to grow the particles observed at Manitou, where the dominant BVOCs emission is actually MBO. The OH oxidation products of MBO are shown to contribute to the local particle growth. The study at Manitou also emphasizes that the contributing organic compounds should have extreme low vapour pressures. The study at the urban site, Beijing, is focused on the contribution of both anthropogenic and biogenic organic compounds to particle growth. The simulation result suggests the ozone oxidation products to contribute mostly to particle growth. (**Paper II to IV**)

- A combination of model was used to assess the climatic impact of hypothetical large methane release to the atmosphere. The impact associated with aerosols and the change in atmospheric composition is shown to be as large as the impact due to the longwave radiative forcing of the elevated methane level. Model SOSAA was applied to assess the feasibility of a geoengineering method which proposes to remove the excess atmospheric methane by raising the NO<sub>x</sub> level. The results suggest that in a scenario where methane level is ten times the present level, doubling NO<sub>x</sub> may reduce the methane life time by 80%. However, the side product of hazardous tropospheric ozone makes this method unfavourable in real life. (**Paper V**).

Atmospheric new particle formation involves a series of complex physical, chemical and dynamical processes that connect atmospheric molecules to particles. Although field observations and laboratory techniques have advanced so far that we can directly study the processes down to the molecular level, these studies are still spatially or temporally limited to serve all our needs. Process based modelling is an alternative approach in addressing the subject. The modelling works in this thesis have also shed light to directions where future research may be conducted. Knowledge gaps in e.g. sulphuric acid production, OH budget as well as emission inventories for both biogenic and anthropogenic organic compounds are waiting for further study. Exact mechanisms driving atmospheric new particle formation are worth searching for. The increased understanding can in practice improve process parameterizations that ultimately strengthen our ability in managing air quality and predicting climate.

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