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

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Natural and anthropogenic aerosols may have a great impact on climate as they directly interact with solar radiation and indirectly affect the Earth's radiation balance and precipitation by modifying clouds. In order to quantify the direct and indirect effects, it is essential to understand the complex processes that connect aerosol particles to cloud droplets. Modern measurement techniques are able to detect particle sizes down to 1 nm in diameter, from ground to the stratosphere. However, the data are not sufficient in order to fully understand the processes. Here we demonstrate how the newly developed one-dimensional column model SOSAA was used to investigate the complex processes of aerosols at a boreal forest site for a six-month period during the spring and summer of 2010. Two nucleation mechanisms (kinetic and organic) were tested in this study, and both mechanisms produced a good prediction of the particle number concentrations in spring. However, overestimation of the particle number concentration in summer by the organic mechanism suggests that the OH oxidation products from monoterpenes may not be the essential compounds in atmospheric nucleation. In general, SOSAA was correct in predicting new particle formation events for 35% of the time and partly correct for 45% of the time.

Introduction

Aerosols have the potential to change the climate regionally and globally as they directly affect the Earth's radiative balance by scattering or absorbing sunlight, and indirectly affect the radiative balance as well as the hydrological cycle by modifying clouds (e.g. Lohmann and Feicher 2005, Kerminen *et al.* 2005). One important phenomenon associated with the atmospheric aerosol system is the new particle formation (NPF) (Kulmala *et al.* 2004b). In an event of the NPF, atmospheric nucleation or the formation of stabilized clusters occurs first. Then the growth of the formed clusters is enhanced by activation of organic vapours which produces 3 nm particles.

Particles grow further to 50–100 nm in diameter by condensation and coagulation (Kulmala *et al.* 2013). At the same time, all particles are experiencing removal by deposition and coagulation with the pre-existing aerosol particle population (Kulmala *et al.* 2004b, Kulmala and Kerminen 2008, Kerminen *et al.* 2010).

The number of observations demonstrating the frequent occurrence of new-particle-formation events has been increasing during the last decade. This enhanced the pressure to understand the phenomenon explicitly (Kulmala *et al.* 2004c). For this reason, sophisticated aerosol dynamical models have been developed, such as the University of Helsinki Multicomponent Aerosol model (UHMA) (Korhonen *et al.* 2004, Vuollekoski *et al.* 2010a, 2010b). Model investigations conducted so far have relied on both zero-dimensional box models (e.g. Gaydos *et al.* 2005) and one-dimensional boundary-layer models (e.g. Boy *et al.* 2006, Hellmuth 2006). Despite increasing uncertainties with increasing spatial scales, aerosol formation has also been modelled using global and regional air-chemistry and air-quality models (e.g. Fan *et al.* 2006, Sotiropoulou *et al.* 2006, 2010, Murphy and Pandis 2009, Merikanto *et al.* 2009, 2010, Makkonen *et al.* 2012a, 2012b). All these studies have clearly demonstrated that atmospheric aerosol formation is a globally important phenomenon that needs to be taken into account when investigating the role of aerosol particles as part of the climate system (Wehner *et al.* 2005, Hussein *et al.* 2008, Kulmala and Kerminen 2008, Manninen *et al.* 2010).

At present, it is not clear which mechanisms drive nucleation in the atmosphere. However, sulphuric acid (H_2SO_4) is believed to be a key player in the nucleation process (e.g. Nieminen *et al.* 2009). Based on atmospheric observations, the best relation between the nucleation rate (J) and the sulphuric acid concentration is suggested to be $J \sim H_2SO_4^n$, where the exponent n is between 1 and 2 (Weber *et al.* 1997, Kulmala *et al.* 2006, Riipinen *et al.* 2007, Kuang *et al.* 2008, Paasonen *et al.* 2009, Sipilä *et al.* 2010). In models, the values of $n = 1$ (activation mechanism) and $n = 2$ (kinetic mechanism) are used most commonly.

Besides H_2SO_4, direct evidence on the participation of organic compounds in the nucleation process has also been found both in laboratory experiments and field observations (Kulmala *et al.* 1998, O'Dowd *et al.* 2002, Zhang *et al.* 2004, 2009, Metzger *et al.* 2010, Kirkby *et al.* 2011). The proposed mechanism is either a "homogeneous heteromolecular nucleation" between sulphuric acid and organic vapour molecules, or one of these two vapours activating the clusters composed of the other vapour molecule (Paasonen *et al.* 2010). However, until now we do not know exactly which organic compounds participate in the nucleation process. The latest results from the CLOUD (Cosmics Leaving Outdoor Droplets) chamber at the European Organization for Nuclear Research, as well as the measurements carried out at the Hyytiälä boreal forest research station, have confirmed that oxidised organic compounds are involved in both the formation and growth of particles under ambient conditions (Schobesberger *et al.* 2013). The CLOUD chamber experiments suggested also that amines are important for the particle formation under anthropogenic influence (Kirkby *et al.* 2011, Almeida *et al.* 2013). In this study, we refer to the mechanism involving sulphuric acid and organic compounds as "organic nucleation".

The freshly-nucleated clusters have rather short lifetimes due to their coagulation with larger particles. As a result, it is the competition between the particle growth and their scavenging by larger pre-existing particles that determines the actual production rate of newly observable particles, regardless of the nucleation mechanism (Kulmala and Kerminen 2008). Although sulphuric acid condenses onto particles, this process is far too slow to explain measured atmospheric growth rates (Boy *et al.* 2003, Kuang *et al.* 2010, Sipilä *et al.* 2010, Kulmala *et al.* 2013). Various field measurements and model simulations have suggested condensation of organic species as the main process responsible for the particle growth, particularly in regions where biogenic volatile organic compound emissions are high (e.g. Kerminen *et al.* 2000, Sellegri *et al.* 2005, Boy *et al.* 2005, Allan *et al.* 2006, Laaksonen *et al.* 2008).

Techniques for measuring ambient sulphuric acid have been available for about two decades (Eisele and Tanner, 1993, Berresheim *et al.* 2000, Petäjä *et al.* 2009), and those for measuring organic compounds have been developing fast.

For example, extremely low-volatility organic compounds have recently been detected (Ehn *et al*. 2012). With our current knowledge of the aerosol precursor gases (H_2SO_4 and biogenic organic compounds), we aimed to conduct a model study to explore how well we are able to predict the atmospheric new-particle-formation events and where the uncertainties are most significant. For this purpose, an aerosol dynamics module based on the University of Helsinki Multicomponent Aerosol dynamics model (UHMA, Korhonen *et al*. 2004) was implemented into the column model SOSA (Model to Simulate Organic Vapours and Sulphuric Acid; Boy *et al*. 2011). SOSA is a model that explicitly resolves the boundary flow over a forest canopy, estimates biogenic emissions from the canopy and includes a detailed atmospheric chemistry scheme. The SOSA model with UHMA aerosol dynamics module included will henceforth be called SOSAA. Our study presented here is the first application of SOSAA to simulate aerosol dynamics. The targeted modelling domain was chosen to be the Finnish boreal forest site at Hyytiälä, for which the longest data sets of aerosol-dynamic measurements and detailed gas-phase measurements are available. In this study, the model chemistry related to the key components in aerosol formation, including monoterpenes and their oxidation products, the hydroxide radical and sulphuric acid, were validated against field measurements. Aerosol simulations were made using both the kinetic and organic nucleation mechanisms. We aimed to assess the model performance with the mentioned two nucleation mechanisms by studying the characteristics of the nucleation mode particles, particle growth, as well as the frequency of new particle formation events.

Material and methods

Model description

SOSAA is a one-dimension chemical-transport model constructed to study the emissions, transport, chemistry and aerosols in the planetary boundary layer in and above a forest canopy. The emission module in the model is based on MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther *et al*. 2006). The chemical mechanistic information was taken from the Master Chemical Mechanism, MCM v3.2 (Jenkin *et al*. 1997, Saunders *et al*. 2003, Jenkin *et al*. 2012; *see* http://mcm.leeds.ac.uk/MCM); for a detailed model description *see* Boy *et al*. (2011). The meteorology performance of SOSAA has been tested against field measurements from Hyytiälä. The model has also been applied in several chemistry studies (Kurtén *et al*. 2011, Mogensen *et al*. 2011, Boy *et al*. 2013).

The aerosol module in SOSAA is based on the aerosol dynamics model UHMA, which is a sectional box model developed for studies of tropospheric new particle formation and growth in clear sky conditions. It has all basic aerosol processes, including nucleation, condensation, coagulation and deposition. In the model, particles are assumed to be spherical and to consist initially of sulphuric acid, water and organic compounds. The inputs include an initial size distribution, ambient temperature, relative humidity and precursor gas concentrations. UHMA has incorporated particle coagulation and multicomponent condensation with a revised treatment of condensation flux onto free molecular regime particles (Lehtinen and Kulmala 2003). The onset of low or semi-volatile organic vapour condensation onto the nanosize inorganic clusters is determined by the Nano-Köhler theory (Kulmala *et al*. 2004a). The deposition of aerosols is modelled with the vertical mixing scheme in the SOSAA model.

SOSAA is written in Fortran with the MPI parallel libraries. Chemistry and aerosol dynamics in each layer of the atmosphere can be calculated in parallel. Simulating one month with approximately 8000 chemical reactions and aerosol dynamics takes about 5 hours runtime, using 32 processor cores of a cluster computer.

The required model inputs can be divided into four different types. The first group includes the characteristics of the area over which the calculations are performed. These include the vertical characteristics of the vegetation such as leaf density, photosynthetic characteristics, etc. The second group consists of meteorological parameters such as radiation conditions, vertical profiles of wind speed, temperature, relative humidity and passive scalars. The model is adjusted to use

information regarding the wind speed, temperature and humidity obtained from synoptic levels as boundary conditions for the upper border of the column. The third group includes inorganic gas concentrations, such as CO and SO_2, and the condensation sinks. These parameters are read in every half an hour with a linear interpolation in between (Boy *et al.* 2011). Typical values of the inorganic gas concentrations above the mixing layer are taken as the upper boundary condition. The last group is the measured particle number size distribution. The particle number size distribution at each model layer is initialised only once a day at midnight. According to a previous study, the nighttime boundary layer height in summer in Hyytiälä can be as low as 200 meters (Ouwersloo *et al.* 2012). Vertical observations from Hyytiälä (M. Boy unpubl. data) suggest that particle number concentrations decrease by a factor of 10 during night. In the early morning hours before the evolution of the boundary layer, there is a strong gradient in the total particle number concentration between the stable surface layer and the residual layer with a factor of up to 10. For this reason, the model layers below 200 m were initialised against ground measurements at midnight. For model layers above 200 m, one tenth of the measured concentrations were used as the midnight initial values.

Model setup

Chemistry scheme

We included all relevant chemistry from MCM for this study (1854 chemical species and 7465 reactions). The reaction rates of Criegee Intermediates from isoprene with sulphur dioxide (SO_2) and water were taken from Welz *et al.* (2012). The reaction rates of Criegee Intermediates from α-pinene, β-pinene (same rate as α-pinene) and limonene with SO_2 were taken from Mauldin *et al.* (2012).

Emission estimates

The emissions of organic vapours from the canopy were calculated with an approach based on the MEGAN model. The variations of emissions are assumed to be driven by two factors: (i) the incident direct and diffuse solar radiation on sunlit and shaded leaves at different canopy levels, and (ii) leaf temperatures at different canopy levels. More information can be found in Guenther *et al.* (2006) who describe the MEGAN model. A detailed description of implementing MEGAN in the SOSAA model can be found in Smolander *et al.* (2013).

Nucleation parameterization

Kinetic and organic nucleation mechanisms were used in this study. The nucleated particles were added to the first size bin (at 2 nm) in the model. In the kinetic mechanism, two sulphuric acid molecules collide to form a cluster as in the kinetic gas theory. Some of the formed clusters will break apart, but some will remain stable. The stable clusters will then grow to particles. The nucleation rate is related to the sulphuric acid concentration, $[H_2SO_4]$, as follows:

$$J_{kin} = k_{kin}[H_2SO_4]^2 \qquad (1)$$

where k_{kin} is the kinetic 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).

The recent results from the CLOUD chamber experiments showed that in ambient conditions monoterpene oxidation products cluster directly with a single sulphuric acid molecule (Schobesberger *et al.* 2013). For this reason, in the case of simulations with the organic nucleation mechanism, the sum of the first stable oxidation products from reactions between OH and monoterpenes (α-pinene, β-pinene, and limonene) were chosen as the nucleating compounds. The nucleation rate is related to the concentrations of sulphuric acid and oxidised organic vapours, [org], as (Paasonen *et al.* 2010):

$$J_{org} = k_{org}[H_2SO_4][org] \qquad (2)$$

where k_{org} is the nucleation coefficient for organic nucleation mechanism.

Growth parameterization

Besides H_2SO_4, organic condensing vapours in the model were based on the stable first reaction products from the hydroxide radical (OH), ozone (O_3) and nitrate (NO_3) oxidation of monoterpenes. According to previous studies, only a fraction of the oxidation products is contributing to condensation (Boy *et al*. 2006, Lauros *et al*. 2011). For this reason, a sensitivity study was carried out and 20% of the oxidation products provided the best agreement with the measurements.

The site of interest: SMEAR II

All the needed input data for the model except for the boundary-layer conditions were from the Station to Measure Ecosystem–Atmosphere Relation (SMEAR II) located in Hyytiälä, a boreal forest site in southern Finland (61°51′N, 24°17′E, 181 m a.s.l.). The vegetation at the station consists mainly of coniferous trees. Two sawmills and a pellet factory around 15 km away may occasionally influence the air masses arriving at SMEAR II. The city of Tampere is 60 km to the southwest of SMEAR II. A more detailed description of the station and the instrumentation is given by Hari and Kulmala (2005) and at http://www.atm.helsinki.fi/SMEAR/.

The temperature, relative humidity and wind speed at the upper boundary of the model column were retrieved from ECMWF Interim Reanalysis database every sixth hour.

The measured H_2SO_4, OH and monoterpene concentrations were used to validate the modelled chemistry. The H_2SO_4 and OH concentra-tions were measured using the Chemical Ionization Mass Spectrometer (CIMS; Petäjä *et al*. 2009), and monoterpene concentrations were measured using the Proton Transfer Reaction-Mass Spectrometry (PTR-MS; Rinne *et al*. 2005, Taipale *et al*. 2008). Some of the gas measurements were obtained from the HUMPPA-COPEC intensive field measurement campaign in summer 2010 (Williams *et al*. 2011). In order to verify our simulations related to particles, measurements of number concentration size-distributions of 3–1000 nm particles by the Differential Mobility Particle Sizer (DMPS; Aalto *et al*. 2001) were used. The DMPS is being operated continuously at SMEAR II.

Simulations were carried out for spring and summer (March–August) of 2010. Unless otherwise mentioned, the following analysis excluded the days that were under anthropogenic influence (Table 1).

# Results and discussion

The modelled precursor gases

The performance of the SOSAA model in reconstructing the emissions, transport and chemistry in the atmospheric boundary layer (ABL) has been verified as reliable (Boy *et al*. 2011). We present here the modelled concentrations of OH, H_2SO_4 and monoterpenes for the summer of 2010 because they are thought to be the key gases related to new particle formation. Monoterpenes were chosen also because the pine forest in Finland is mainly a monoterpene emitter (Rinne *et al*. 2007, 2009, Hakola *et al*. 2012).

Table 1. Days omitted from the analysis due to reasons given.

Days omitted	Reason
Influential air mass to Hyytiälä	
13–15 July	Pollution plume advected from the southwest of the site possibly from Tampere
18 July	High monoterpene concentrations detected due to sawmill operation
26–30 July	Strong peaks in SO_2 and pentane detected due to biomass burning emissions
3–4 August	High monoterpene concentrations detected due to sawmill operation
6–10 August	High monoterpene concentrations detected due to sawmill operation
Incomplete model input data	
23–31 May	SO_2 measurement not available
3 and 15 June	Bad data from the DMPS instrument
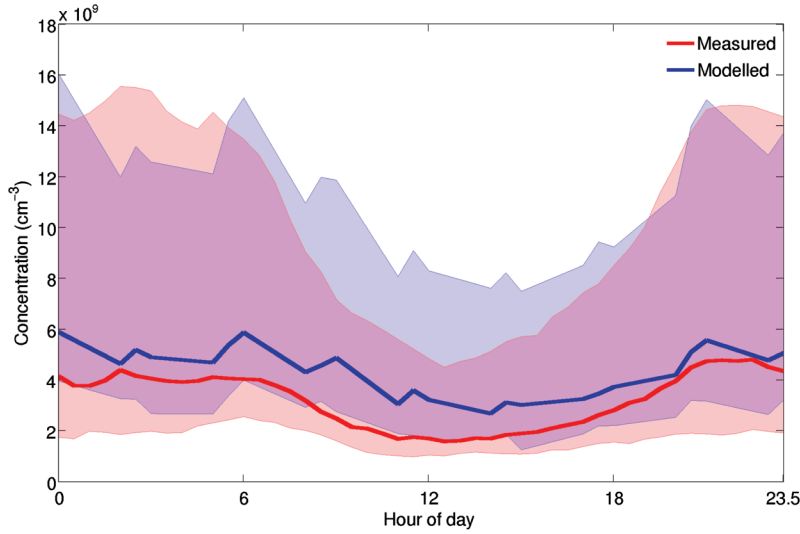
Fig. 1. Median diurnal variation of the measured and modelled monoterpene concentration. The upper and lower borders of the shaded areas are the 75 and 25 percentiles of the measured and simulated data sets.
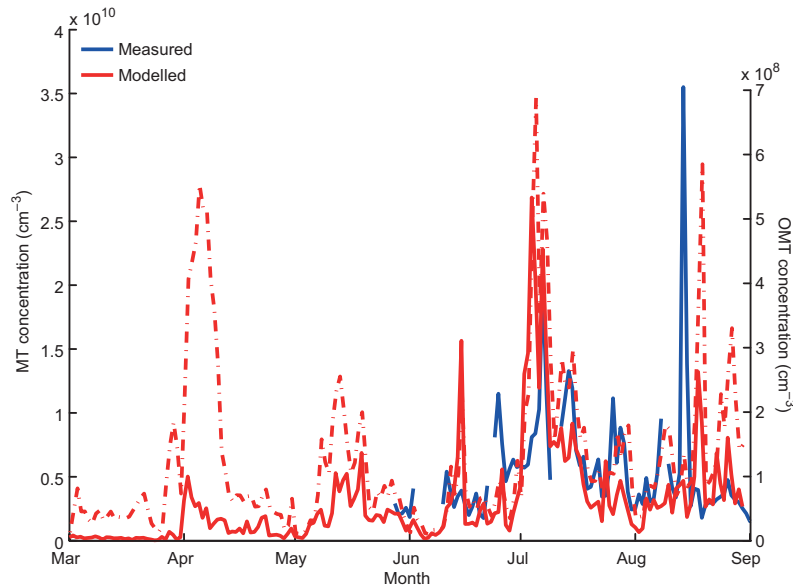
Fig. 2. Daily medians of the measured (solid blue line) and modelled (solid red line) concentrations of monoterpenes (MT, left-hand-side y-axis), and modelled (dashed red line) concentration of oxidation products from monoterpenes (OMT, right-hand-side y-axis).

In general, the modelled monoterpene concentrations agreed well with the measurements (Fig. 1). During daytime, the modelled concentrations were slightly lower as compared with the measurements. One reason for this is that the oxidants in the model were overestimated for the daytime (specifically OH, *see* explanation below). Another reason is that no anthropogenic influence was included in the model. During the HUMPPA-COPEC campaign, air masses advected mostly from the southwest (54% of the time) and less from the southeast (21%) and northwest (10%). A regional 50-km-wide surface cover analysis showed that the anthropogenic influence was more prominent in the south (SE and SW) than in the northwest (Williams *et al*. 2011). Besides, we cannot eliminate the possibility that the vertical mixing in the model was slightly overestimated for the daytime, which would lower the concentrations of monoterpenes under the forest canopy.

When comparing the daily medians of the measured and modelled monoterpene concentrations, we also see that the agreement was good in general, but with few exceptions (Fig. 2). The modelled monoterpene concentrations varied

Fig. 3. Median diurnal variation of the measured OH concentration at 2 m and modelled OH concentration at 20 m. The upper and lower borders of the shaded areas are the 75 and 25 percentiles of the measured and simulated data sets. The model height of 20 m was chosen for the comparison because the measurements were conducted at a cleared site which was exposed to sunlight.
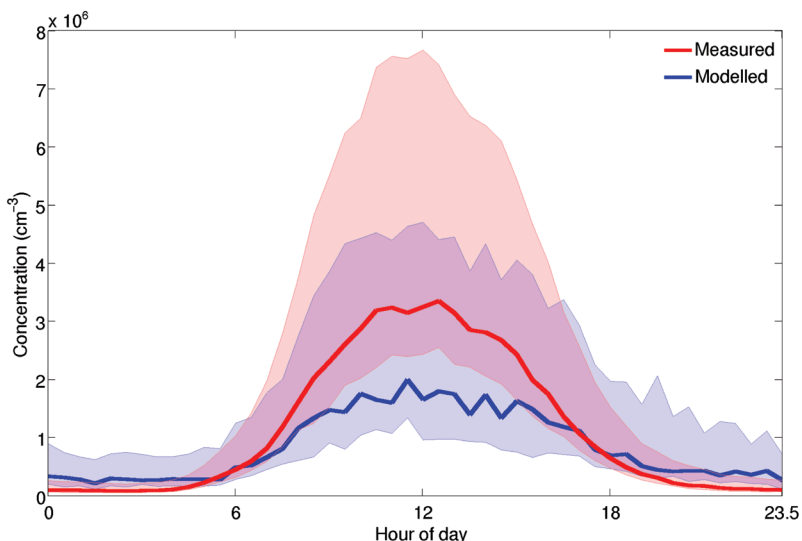
between 2×10^9 and 1.5×10^{10} cm^{-3}. On 14 June it was raining at the station, and this most likely affected the monoterpene concentrations in the air. Because precipitation is not implemented in our model simulations, this is one source of the difference between the measurements and model results. 14 August was cloudy and possibly affected by air masses from the south where the city of Tampere is located. However, the model does not include input from human activities. Since the first stable products from monoterpene oxidation reactions were involved in the following aerosol simulations, we checked also their daily-median concentration. The concentration varied between 10^7 and 10^8 cm^{-3} and was strongly associated with the monoterpene concentration.

As compared with the measurements, the diurnal variation of the modelled OH concentration was greater in summer (Fig. 3). The underestimation for nights could result from the missing recycling mechanism of OH by organic compounds (Lelieveld *et al.* 2008, Taraborrelli *et al.* 2009). The modelled OH concentration was slightly higher than the upper limit of the measurement uncertainty (+50%) at summer noon. This result is consistent with a previous study, which reported a missing OH reactivity of more than 60% during daytime (Mogensen *et al.* 2011). Besides, since the model setup assumed a homogeneous pine forest for Hyytiälä, the model

missed other organic compounds emitted by trees other than pines. Mogensen *et al.* (2011) also pointed out that monoterpenes could only explain about 10% of the OH reactivity in Hyytiälä.

The modelled H_2SO_4 concentration was lower than the measurements for most of the time (Fig. 4). Since the SO_2 oxidation by OH was the dominant source for H_2SO_4 in the model, the diurnal concentration pattern of H_2SO_4 followed that of OH closely. At night, when the OH concentration was approximately one to two orders of magnitude lower than during daytime, the H_2SO_4 level was also very low. However, even though the model overestimated the OH concentration for the daytime, the H_2SO_4 concentration was still lower than the measured one by about 50%. The chemistry scheme in our runs included the newest Criegee Intermediates reaction rates. The deficiency here implies that there could be other unknown sources of atmospheric H_2SO_4. After all, a 50% deficiency is a fairly good result, since the error estimation for the CIMS H_2SO_4 measurement ranges typically from 30% to 60% (Plass-Dülmer *et al.* 2011).

Modelling of new particle formation events

The mechanisms of nucleation are currently not fully understood. As a first application of the
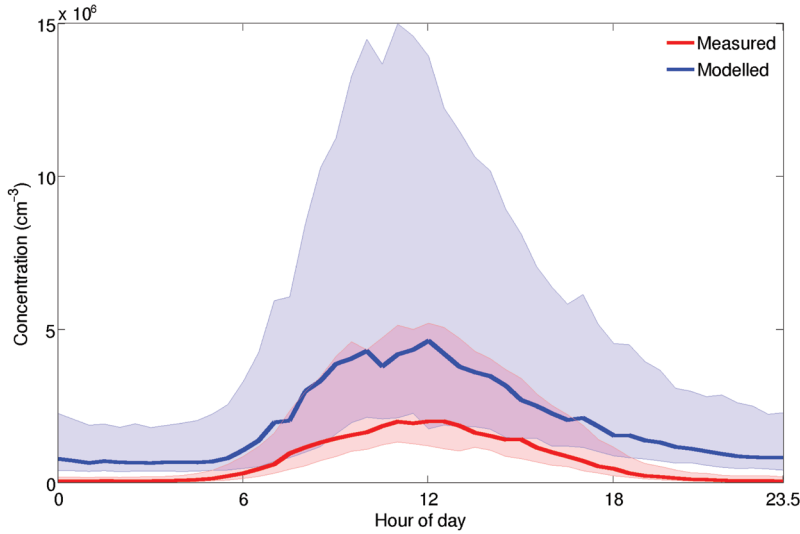
Fig. 4. Median diurnal variation of the measured H_2SO_4 concentration at 2 m and modelled H_2SO_4 concentration at 20 m. The upper and lower borders of the shaded areas are the 75 and 25 percentiles of the measured and simulated data sets. The model height 20 m was chosen for the comparison because the measurements were conducted at a cleared site which was exposed to sunlight.
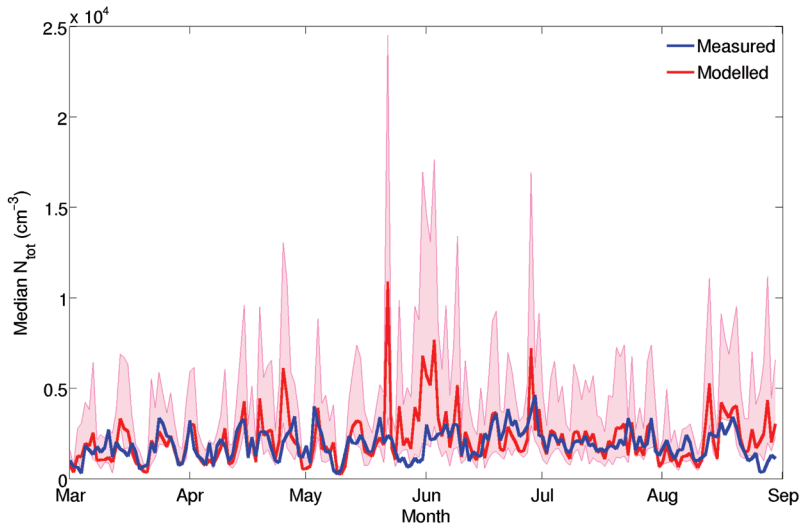
Fig. 5. Daily medians of the total particle number concentration, N_{tot}, based on measurements and model simulation assuming the kinetic nucleation mechanisms with $k_{kin} = 7 \times 10^{-14}$ cm^3 s^{-1}. The upper and lower borders of the shaded area represent model simulations with $k_{kin} = 1.4 \times 10^{-13}$ cm^3 s^{-1} and $k_{kin} = 1.4 \times 10^{-12}$ cm^3 s^{-1}, respectively. The days listed in Table 1 are not filtered out in this figure.

model with the aerosol dynamics module, simulations of aerosol size distributions were done for the spring and summer of 2010 with the kinetic and organic nucleation mechanisms.

Sensitivity test of nucleation coefficients

In order to find suitable nucleation coefficients for the nucleation mechanisms, several runs were performed for kinetic and organic nucleation mechanisms, respectively. In case of the runs with the kinetic nucleation mechanism, we started with the coefficient $k_{kin} = 1.4 \times 10^{-12}$ cm^3 s^{-1}, as suggested

by Paasonen *et al.* (2010). Then three more runs were performed with the coefficient decreased by a factor of 10, 20 and 100. The value of $k_{kin} = 7 \times 10^{-14}$ cm^3 s^{-1} gave the best agreement for the total particle number concentration (Fig. 5). The agreement was reasonably good except for late May. During this period (23–31 May) no SO_2 measurements were available, so we used a prescribed SO_2 concentration based on a forward and backward gap-filling technique, which turned out to give too high SO_2 concentrations for most of the period. As mentioned before, SO_2 influences the sulphuric acid concentration in the model and has therefore a strong effect on the number con-

Fig. 6. Daily medians of the total particle concentration, N_{tot}, based on measurements (blue line) and model simulation assuming on organic simulation with $k_{org} = 1.1 \times 10^{-13}$ cm^3 s^{-1} (red line). The upper and lower borders of the shaded area represent model simulations with $k_{org} = 1.1 \times 10^{-12}$ cm^3 s^{-1} and $k_{org} = 1.1 \times 10^{-14}$ cm^3 s^{-1}, respectively. The days listed in Table 1 are not filtered out in this figure.
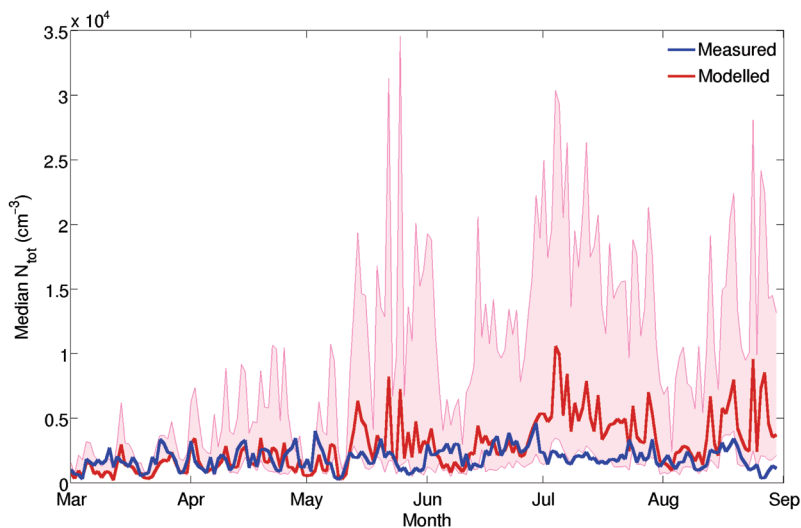

centration of newly-formed particles in the kinetic nucleation mechanism.

In case of organic nucleation, the value of the nucleation coefficient $k_{org} = 1.1 \times 10^{-13}$ cm^3 s^{-1} suggested by Paasonen *et al*. (2010) gave the best estimation for the total particle number concentration (Fig. 6). The agreement was good in spring until mid-May. From mid-May onwards, the model tended to overestimate the particle number concentration. We also noticed that since mid-May, differences between simulated number concentrations increased. Such model behaviour is expected to be related to organic nucleating compounds. The periods when the model overestimated the particle number concentration coincided with the periods when high concentration levels of monoterpenes were predicted by the model (Fig. 2). These periods occurred especially in July. However, the modelled monoterpene concentrations were not necessarily high compared to the available measured monoterpene concentrations in the summer of 2010. The organic nucleation mechanism turned out to overestimate the particle concentration in the summer when the organic nucleating compounds were abundant. For this reason we doubt whether the oxidation products from monoterpenes and OH were the main compounds participating in nucleation at the Hyytiälä forest site.

When studying the particle number size distribution, it is a tradition to classify each day as a new particle formation event day, non-event day, or undefined day using a classification scheme introduced by Dal Maso *et al*. (2005). We carried out the classification for the measurements, as well as for the simulations with the kinetic nucleation coefficient $k_{kin} = 7 \times 10^{-14}$ cm^3 s^{-1} and organic nucleation coefficient $k_{org} = 1.1 \times 10^{-13}$ cm^3 s^{-1}. In order to study the model behaviour of new particle formation events, we defined so-called "good days" as the days when both the measurements and simulation indicated an event and particles grew to similar sizes, as well as the days when a non-event was classified in both measurements and model simulations. The "good" days were found to be the same for the simulations with the same nucleation mechanism, but not for the simulations with a different nucleation mechanism. In case of the 35 event days recorded during the spring and summer of 2010, the model simulated 20 "good" event days with the kinetic nucleation mechanism and only 7 "good" days with the organic nucleation mechanism. Therefore, the kinetic nucleation mechanism had a better performance in reproducing the event days as compared with the organic nucleation mechanism.

From the averaged one-day number size distribution of all "good" days, the value of $k_{kin} = 7 \times 10^{-14}$ cm^3 s^{-1} gave the best agreement with the measurements among all the kinetic simulations (Fig. 7). In both measurements and simulations, the background particle concentrations slowly decreased during night. New particle formation started, on average, around noon and particles
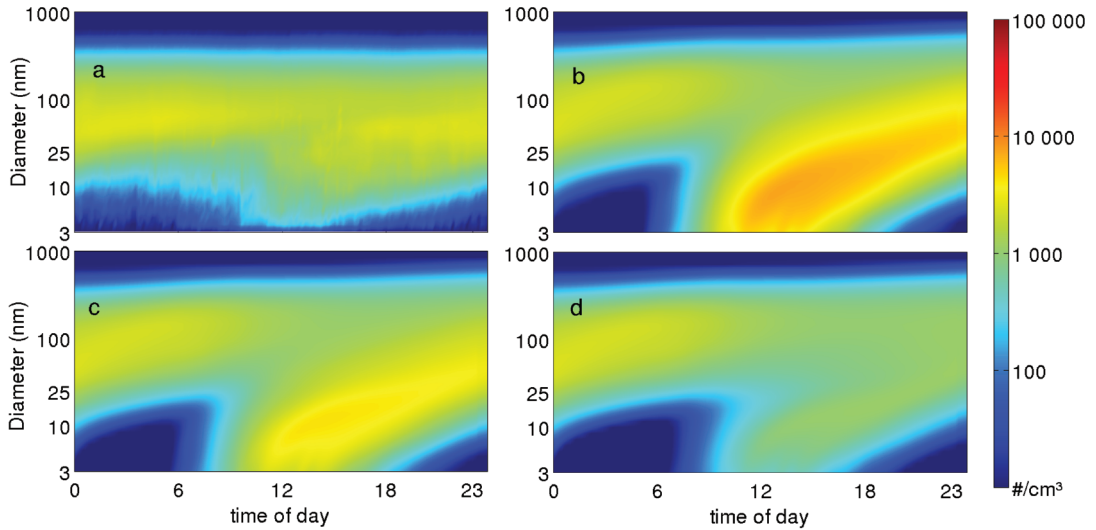
Fig. 7. Averaged one-day number size distributions from "good" days based on (**a**) measurements, (**b**) model simulation assuming the kinetic nucleation mechanism with $k_{kin} = 1.4 \times 10^{-13}$ cm³ s⁻¹, (**c**) model simulation assuming the kinetic nucleation mechanism with $k_{kin} = 1.4 \times 10^{-14}$ cm³ s⁻¹, and (**d**) model simulation assuming the kinetic nucleation mechanism with $k_{kin} = 1.4 \times 10^{-15}$ cm³ s⁻¹.

continued to grow into sizes similar to the background particles by the end of the day. During some individual event days, the particle formation started earlier than noon. The best value of k_{kin} for the kinetic nucleation mechanism determined in our simulations was 20 times smaller than the value suggested by Paasonen *et al.* (2010) in their analysis of the Hyytiälä data from 2007–2009, but the year modelled in this study was 2010. The summer of 2010 was warmer and had a higher proportion of southerly air mass flow than in the previous years (Williams *et al.* 2011). The difference in meteorological conditions may contribute to differences in the values of the nucleation coefficients.

The averaged one-day number size distributions of "good" days in the simulations with the organic nucleation mechanism had a very similar behaviour as in the simulations with the kinetic simulation mechanism. The best case for the organic simulation was indeed with the value of $k_{org} = 1.1 \times 10^{-13}$ cm³ s⁻¹ as suggested by Paasonen *et al.* (2010).

Simulation of particle concentrations

Based on the sensitivity studies presented above,

the best values of the nucleation coefficients were $k_{kin} = 7 \times 10^{-14}$ cm³ s⁻¹ and $k_{org} = 1.1 \times 10^{-13}$ cm³ s⁻¹ for the spring and summer of 2010. In the following analysis, only these two values will be used.

Particles with diameters between 3 and 25 nm are usually classified as nucleation-mode particles. We studied the median diurnal variation of the nucleation mode particle concentration during the "good" days mentioned earlier. The simulation with the kinetic mechanism gave a median diurnal pattern of nucleation mode particles similar to that in the measurements (Fig. 8). Starting with the same background particle distribution at midnight, the nucleation-mode particles in the model decreased faster than in reality, so there were fewer particles in the model than what was measured in the early morning. One explanation could be that the model overestimated the deposition, so that the particle concentration decreased fast without a production term during night. The modelled nucleation-mode particle number concentration started to increase after reaching its minimum at around 06:00, reaching a maximum at around 14:00. The modelled concentration increase was slightly faster than the measured one during morning. The modelled and meas-
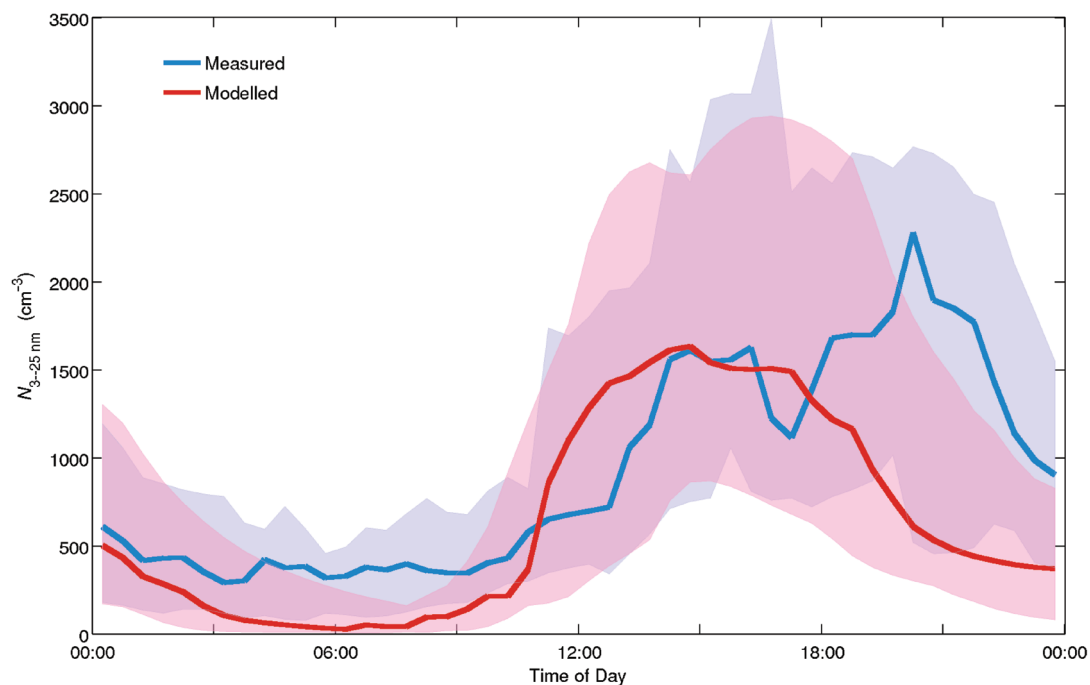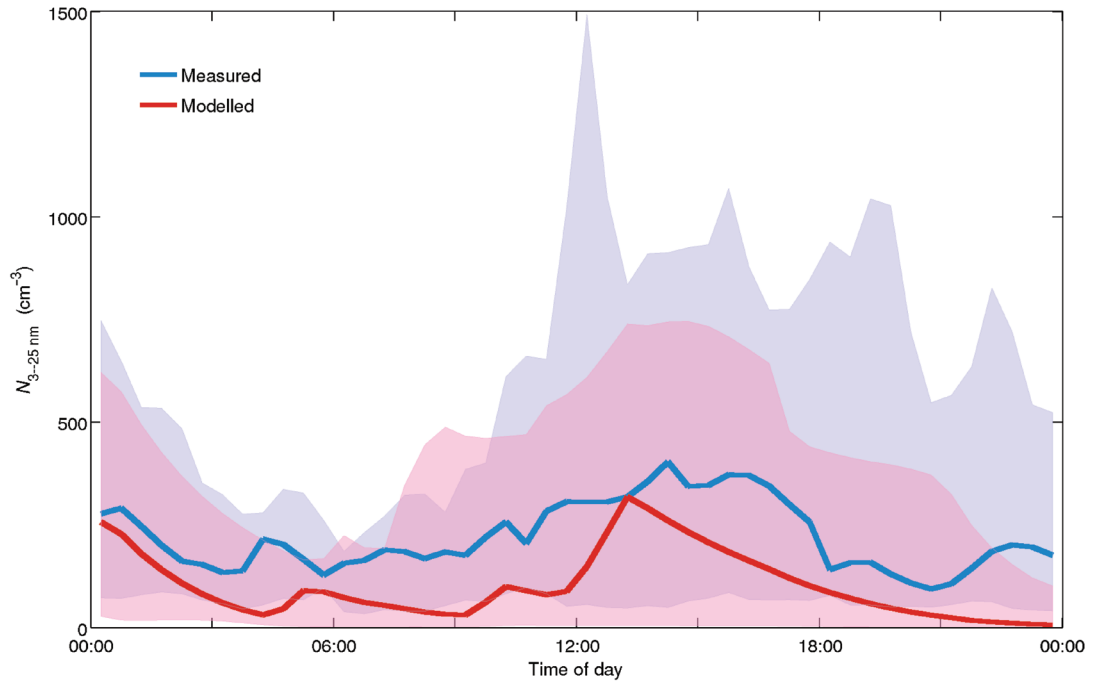
Fig. 8. Median diurnal profile of the nucleation mode (3–25 nm) particle concentration, N_{nuc}, based on measurements (blue line) and model simulations assuming the kinetic simulation with $k_{kin} = 7 \times 10^{-14}$ cm³ s⁻¹ (red line). The upper and lower borders of the shaded areas are the 75 and 25 percentiles of the measured and simulated data sets.

ured nucleation-mode particle number concentrations reached similar levels at about noon. The modelled concentration decreased after 14:00, whereas the measurements showed another peak concentration in the early evening.
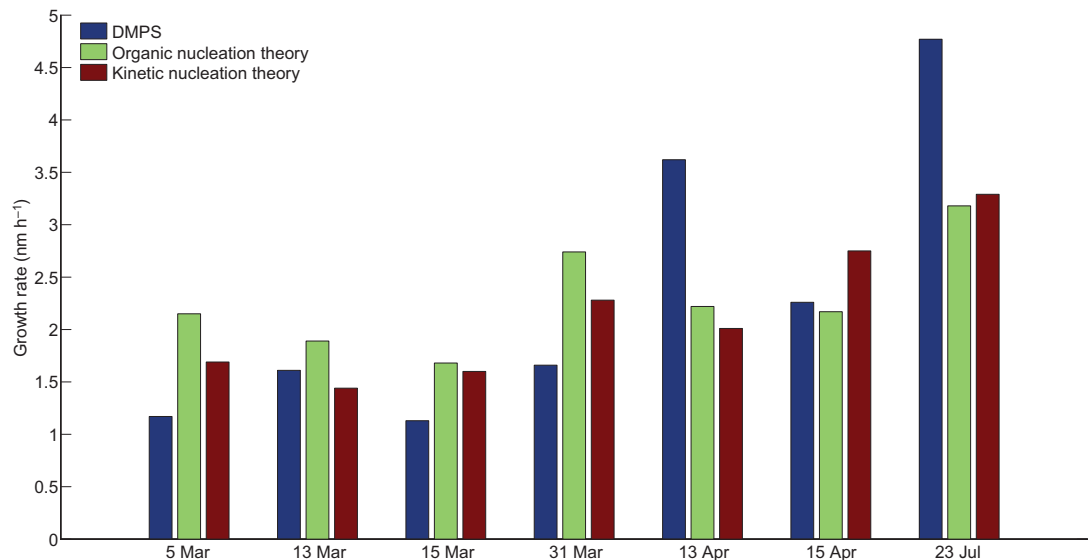
The simulation with the organic nucleation mechanism produced a relatively similar median diurnal variation for nucleation mode particles as did the kinetic nucleation mechanism (Fig. 9). The difference was that the modelled particle number concentration did not vary as strongly for the organic nucleation mechanism. In both the kinetic and organic simulations, the nucleation mode particle number concentration decreased earlier than what was observed after reaching the maximum in the afternoon. One possible explanation for this might be that the modelled growth of particles was either too low or too high in the afternoon and during night. There were seven days, for which the particle growth rates could reliably be determined from the measurements, and for these days the modelled growth rates were comparable with the measured ones (Fig. 10). However, for 13 April and 23 July the modelled growth was slower. On both these days, the air masses entering Hyytiälä were shifting toward the clean northwest, which may have brought a very clean background for particles to grow. The model simulations did not include such air mass change, so the growth of particles for these two days was slower than in reality because some of the condensing vapours were consumed by unrealistically high number of background particles in the model. We also noted that no matter which nucleation mechanism was used, the modelled growth rates were close to each other, with differences below 20%. So the discrepancy in nucleation mode particle number concentrations in the afternoon and night is likely to be due to the overestimated downward flux and deposition of particles in the model. Advection of polluted air masses to the measurement site could also contribute to the error.

Scatter plots of nucleation mode (3 to 25 nm) particles (Fig. 11) indicate that the SOSAA

Fig. 9. Median diurnal profile of the nucleation mode (3 to 25 nm) particle concentration, N_{nuc}, based on measurements (blue line) and model simulations assuming the organic simulation with $k_{org} = 1.1 \times 10^{-13}$ cm^3 s^{-1} (red line). The upper and lower borders are the 75 and 25 percentiles of the measured and simulated data sets.

Fig. 10. Growth rates of nucleation mode (3 to 25 nm) particles calculated from DMPS measurements and simulations with organic/kinetic nucleation mechanism. Data points are only drawn for the observed event days.

model tended to overestimate the nucleation-mode particle number concentration during midday and underestimate it during nighttime.

We know that low temperatures at night may cause a strong inversion in the model, which causes an overestimation of deposition of back-
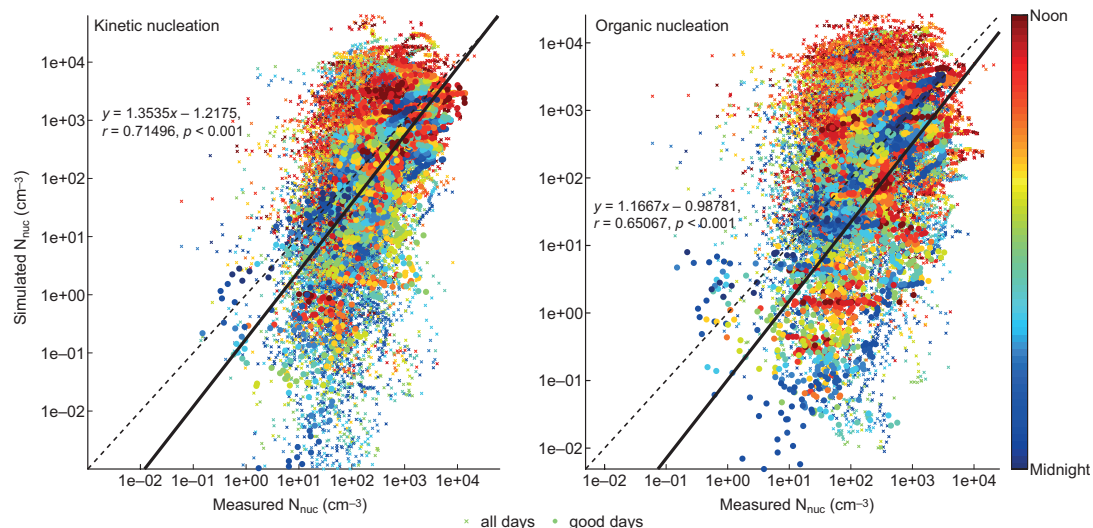
Fig. 11. Modelled (*y*-axis) *vs*. measured (*x*-axis) number concentrations of nucleation mode (3–25 nm) particles, N_{nuc}, for the whole simulation period. Data points for the "good" days are dots while other data points are crosses. All points are coloured according to the time of day (*see* the scale on the right). The left-hand-side plot is based on a simulation with the kinetic nucleation mechanism, and the right-hand-side plot is based on a simulation with the organic nucleation mechanism.

ground particles, and that horizontal advection of particles to the site cannot be accounted for in a column model like SOSAA. During daytime, when sulphuric acid and organic-compound concentrations increased rapidly, there were usually more particles in the model simulations than what was measured.

On the "good" days, when the simulations and measurements showed a consistent event classification and similar growth, the agreement between the modelled and measured nucleation-mode particle number concentrations was good for both the kinetic and organic nucleation mechanisms. The kinetic mechanism was, however, slightly better (cf. correlation coefficients, *r*, in Fig. 11).

Model performance

As mentioned before, we performed the event classification for both measurements and model simulations. The model was considered to be "correct" when the classification of the modelled day was consistent with the classification form measurements. Among the "correct" days there were some "good" days when the simulation

matched the measurements well. Let us consider a typical example of a "good" day (Fig. 12), when the measured background particles were diluted at about noon and soon after that new particle formation started. The particles grew rapidly to about 25 nm in about an hour. For the rest of the day, the particles continued to grow slowly up to several tens of nm in diameter. The model took as input the background particle concentration at midnight. The small particles gradually diminished throughout the night until there was a clear background dilution of all particles at around noon. Then new particle formation started and particle growth continued in almost the same way as in reality.

The model was considered to be "wrong" when an event was seen in the measurements, but no event was modelled, or vice versa. There were also "semi-correct" days when we could not determine whether the model was correct or wrong, e.g. an observed non-event or event day was modelled as undefined, or an undefined day was modelled as an event day or non-event day. Most days belonging to this category occurred when an observed undefined day was modelled as an event day (Fig. 13). In the measurements we sometimes saw a burst of particles without
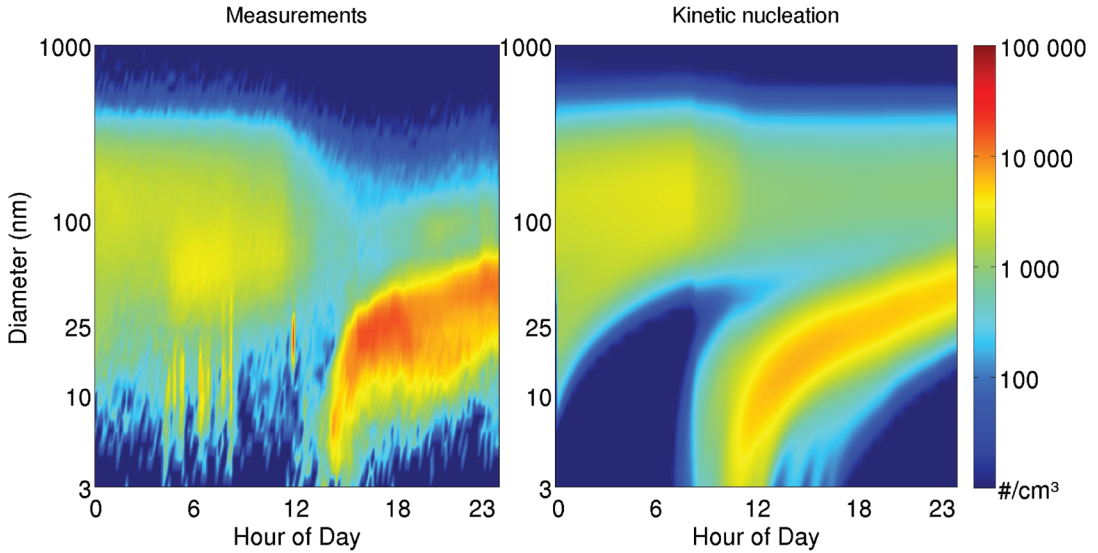
Fig. 12. The time evolution of the particle number size distribution during a "good" day on 13 April based on measurements and simulation assuming the kinetic nucleation mechanism.
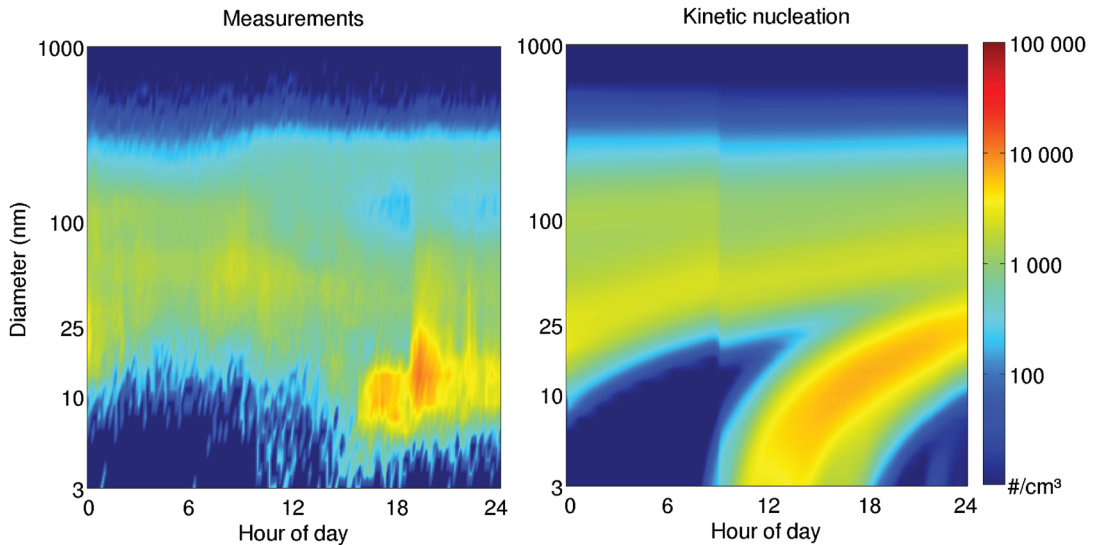

Fig. 13. The time evolution of the particle number size distribution during a "semi-correct" day on 16 March based on measurements and simulation assuming the kinetic nucleation mechanism.

observing the continuous growth of the smallest particles beforehand. One possible explanation for this is that the particles were first formed somewhere else in the forest, e.g. above the canopy, and then transported to the measurement site inside the canopy. If this was indeed the case, the event we saw in the model was then a correct description of the forest area at Hyytiälä in general.

The kinetic and organic nucleation mechanisms seemed to have similar effects on the prediction of new particle formation events. Simulations with both mechanisms were correct for about 35% of the total number of days (Fig. 14). As mentioned earlier, the kinetic nucleation mechanism was slightly better than the organic nucleation mechanism in having more "good" days. It is noteworthy that most of the "good"
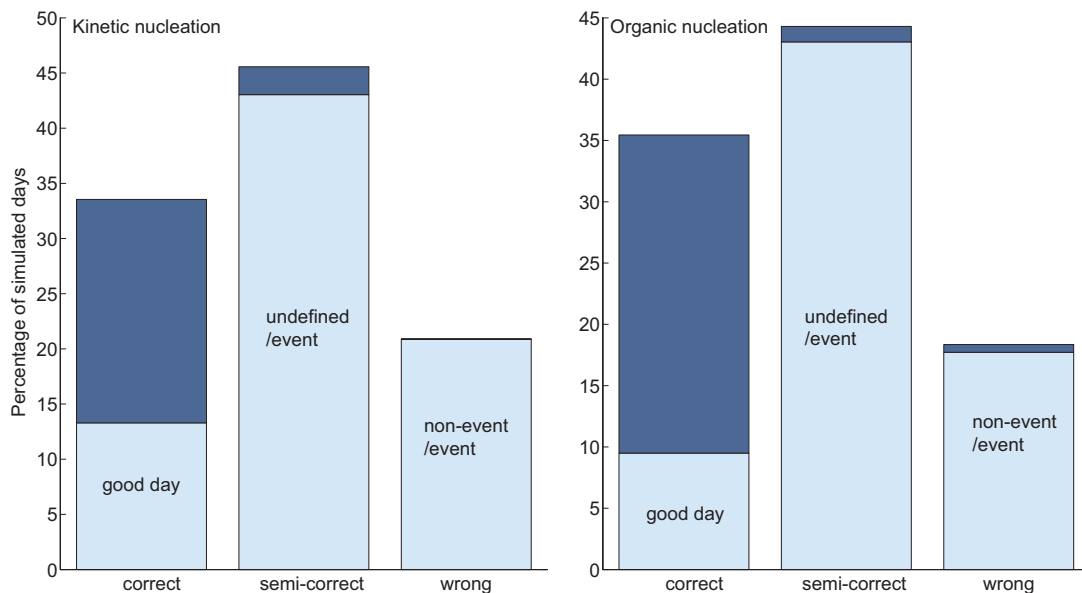
Fig. 14. Statistics of the modelled days based on comparing the event classification between the simulations and observations.

days were in March and April, which is when new particle formation events are most frequent in Hyytiälä. The model was "semi-correct" for about 45% of the time. Most of the "semi-correct" days were due to predicting an event day for an undefined day. On these days, there might have been a lift or shift of measured air masses, but SOSAA was obviously missing such phenomena in the boundary layer due to its limitation as a column model. The model was "wrong" for approximately 20% of the time. This was mostly because an observed non-event day was modelled as an event day. The model tended to have more error in summer than in spring predictions. Since sulphuric acid concentrations did not differ much between spring and summer, while monoterpene concentrations varied a lot, it may be speculated that the OH oxidation products from monoterpenes are not an essential factor for nucleation at Hyytiälä in summer.

Summary and conclusions

The results showed the ability of SOSAA to reconstruct the general behaviour of atmospheric trace gases and new particle formation in a boreal forest environment. The model succeeded in capturing the diurnal variation of the monoterpene concentration. The results agreed with the previous studies in that there is a missing OH reactivity and that the budget of atmospheric sulphuric acid production is not closed.

With the concentrations of the sulphuric acid, monoterpenes and oxidation products from monoterpenes modelled, sensitivity studies were carried out to find the most appropriate nucleation coefficients for the kinetic and organic nucleation mechanisms. The kinetic nucleation coefficient that agreed best with the data was 20 times smaller than the coefficient suggested by Paasonen *et al.* (2010), which reminds us about the uncertainty that the kinetic nucleation mechanism carries. With the best estimates for the nucleation coefficients, both kinetic and organic simulations produced a good prediction of particle number concentrations in spring. However, the organic nucleation mechanism frequently overestimated the particle number concentration in summer when organic nucleating compounds were abundant. This result suggests that oxidation products from monoterpenes and OH reactions may not be the essential compounds in atmospheric nucleation.

We performed event classification for both model simulations and measurements. The two

nucleation mechanisms had a similar performance. The model was correct for 35% of the time, wrong for 20% of the time and semi-correct for 45% of the time. It is interesting to see that in case of the semi-correct time, the model often predicted an event for an observed undefined day. If taking into account that SOSAA is a column model that assumes the modelled area to be horizontally homogeneous, the semi-correct days might represent the cases when new particles had been formed somewhere else in the forest, or above it, and then transported to the measurement site.

There are still many processes to be improved in the SOSAA model, e.g. vertical mixing and deposition of gases and particles, and the growth scheme of particles. At the same time, SOSAA could be a good platform to test new theories or schemes in chemistry, emissions, meteorology and new particle formation. As a column model, SOSAA will also be a good tool for investigating the vertical profile of new particle formation, which will be the next task for our model simulations.

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