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Discussions

The simulations of sulfuric acid concentration and new particle formation in an urban atmosphere in China

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Abstract

Simulations of sulfuric acid concentration and new particle formation are performed by using the zero-dimensional version of the model MALTE (Model to predict new Aerosol formation in the Lower TropospherE) and measurements from the Campaign of Air Quality Research in Beijing and Surrounding areas (CAREBeijing) in 2008. Chemical reactions from the Master Chemical Mechanism Version 3.2 (MCM v3.2) are used in the model. High correlation (slope = 0.72, $R = 0.74$) between the modelled and observed sulfuric acid concentrations is found during daytime (06:00–18:00). The aerosol dynamics are simulated by the University of Helsinki Multicomponent Aerosol (UHMA) model including several nucleation mechanisms. The results indicate that the model is able to predict the on- and offset of new particle formation in an urban atmosphere in China. In addition, the number concentrations of newly formed particles in kinetic-type nucleation including homogenous homomolecular ($J = K[H_2SO_4]^2$) and homogenous heteromolecular nucleation involving organic vapours ($J = K_{het}[H_2SO_4][Org]$) are in satisfactory agreement with the observations. However, the specific organic compounds possibly participate in the nucleation process should be investigated in further studies.

1 Introduction

New particle formation (NPF) events have been observed to take place in diverse atmospheric environments all over the world including the stratosphere, free troposphere, cloud outflows, coastal and marine areas, above and inside the forest, remote continental boundary layers and polluted urban environments (Kulmala et al., 2004b; Kulmala and Kerminen, 2008; Holmes, 2007). Both field measurements and model results show that particle nucleation is a significant source of potential cloud condensation nuclei (CCN), which may influence cloud microphysical and climate-relevant properties (Merikanto et al., 2009; Yue et al., 2011; Wiedensohler et al., 2009; Spracklen et al., 2008). Consequently, advancing our understanding on the formation mechanisms of new particles in the atmosphere has become critically important.

Several nucleation theories such as binary nucleation (Kulmala et al., 1998), ternary nucleation (Napari et al., 2002) and ion-induced nucleation (Yu and Turco, 2000) have been proposed and explored since last century. Gaseous sulfuric acid has been identified as a key precursor in the nucleation process because of its low vapour pressure at typical atmospheric temperatures (Weber et al., 1995; Berndt et al., 2005; Sipilä et al., 2010). In most environments, the relationship between the observed particle nucleation rates and ambient sulfuric acid concentrations with the exponents lies in the range $1 \sim 2$ (Kuang et al., 2008; Riipinen et al., 2007; Sihto et al., 2006; Paasonen et al., 2009; Nieminen et al., 2009). These values indicate the activation (exponent 1) and kinetic (exponent 2) nucleation processes (McMurry and Friedlander, 1979; Kulmala et al., 2006), respectively. Meanwhile, higher power values in Beijing have been reported recently (Wang et al., 2011), implying that thermodynamic process seems to work better than the activation and kinetic nucleation theories.

The presence of sulfuric acid in gaseous concentrations of $10^6 \sim 10^7$ molecules cm^{-3} is necessary in order to observe new particle formation events in the atmosphere (Zhang et al., 2012). However, the measurement of sulfuric acid concentration is difficult to achieve due to the high requirements of technology. The first measurements of atmospheric gaseous sulfuric acid have been performed in the stratosphere using Passive Chemical Ionization Mass Spectrometry (Arnold and Fabian, 1980; Arnold et al., 1982; Arnold and Buhrke, 1983). Although the measurements of sulfuric acid in the lower troposphere have been achieved since last century (Eisele and Tanner, 1993; Weber et al., 1995, 1997), the gaseous sulfuric acid information is still very rare, especially in polluted urban environments.

Several methods have been applied to obtain the sulfuric acid concentration in order to make up the absence of direct measurement. The essential parameterization assumes only one source (chemical reaction between sulfur dioxide and the OH radical) and one sink (condensation onto the pre-existing particles) for sulfuric acid in the atmosphere (Weber et al., 1997; Kulmala et al., 2001). Based on this assumption, Petäjä et al. (2009) developed three proxies for the sulfuric acid concentration and the estimated results correlated well with the observations. However, the proxies might be site-specific. Recent research found a single proxy for the sulfuric acid concentration that can be applied over a greater range of environments (Mikkonen et al., 2011). Nevertheless, this proxy just originates from the statistical analysis and the real chemical process would be covered. Modelling is an adequate possibility to trace the detailed sources and sinks of species in the atmosphere. Several box model simulations have been performed to calculate the sulfuric acid concentrations (Boy et al., 2005, 2006).

However, all these methods were only applied in clean environments partly due to the lack of direct sulfuric acid measurement in the polluted environments. The first gaseous sulfuric acid measurements in Beijing were conducted during the CAREBeijing 2008 campaign (Zheng et al., 2011). Hence, the purpose of this study is to test the MALTE model for Beijing. The sulfuric acid concentration was modelled and the new particle formation event was predicted with various nucleation mechanisms.

2 Materials and methods

2.1 Instrumentation

The sampling site is located on the sixth floor of an academic building on the campus of Peking University (PKU; 39.99° N, 116.31° E). Two major roads with heavy traffics at the east and south of the site are respectively 200 m and 500 m away. Detailed descriptions of the measurement site and surrounding environment can be found in Wu et al. (2008). The PKU site is assumed to be representative of the polluted urban atmosphere.

On-line high-resolution instruments of both gaseous pollutants and aerosol characteristics were carried out simultaneously during the CAREBeijing 2008 campaign, from 12 July to 25 September. A dual mobility particle size spectrometer TROPOS-type TDMPS: Twin Differential Mobility Particle Sizer, consisting of two parallel Hauke-type

Differential Mobility Analyzers (DMAs) was used to measure number size distributions of atmospheric particles from 3 to 900 nm in mobility diameter (Birmili et al., 1999). The relative humidity (RH) within the whole system was kept below 30 % by adding silica-gel dryers both in the inlet line and in the sheath air cycle to avoid condensation of water during humid days. In addition, the particle number size distributions were corrected for particle losses inside the TDMPS and in the sampling configuration, following the method of the "equivalent length" as described in Wiedensohler et al. (2012).

Ambient gaseous sulfuric acid concentration is measured by an AP-ID-CIMS (Atmospheric Pressure Ion Drift – Chemical Ionization Mass Spectrometry) apparatus built by Texas A&M University (Fortner et al., 2004; Zheng et al., 2010). Briefly, the device consists of four major elements including an inlet, an Am-241 ion source, a special ion-drift tube and a quadrupole mass spectrometer. The main proton-transfer reaction is:

$$H_2SO_4 + NO_3^- \cdot HNO_3 \rightarrow HSO_4^- \cdot HNO_3 + HNO_3 \tag{1}$$

Both reagent and product ions are detected sequentially for 12 s. The detection limit of sulfuric acid is as low as 10^5 molecules cm^{-3} with an uncertainty of 36 %.

High time-resolution volatile organic compounds (VOCs) concentrations were obtained using Proton Transfer Reaction – Mass Spectrometer (PTR-MS), which was used for the first time in China. The uncertainties of PTR-MS for various compounds were estimated to 20 % and the detection limits ranged from 20 to 250 ppt (Yuan et al., 2010). In addition, instantaneous whole air samples were taken using fused silica-lined stainless steel canisters (3.2 L, Entech Instrument, Inc., Simi Valley, CA, USA). The samples were quantified by gas chromatograph (GC, HP-7890A, Hewlett Packard Co., Palo Alto, CA, USA) equipped with a quadrupole mass spectrometer (MSD, HP-5975C, Hewlett Packard), and a flame ionization detector (FID). Detailed analytical method and result can be found in Wang et al. (2010).

The photolysis frequencies of O_3 (J_{O^1D}) and NO_2 (J_{NO_2}) were measured by using specifically designed filter radiometers provided by the Research Center Jülich

(Forschungszentrum, FZJ), Germany. The accuracy of the photolysis frequency measurements is estimated to be 10 % at solar zenith angles smaller than 80° (Bohn et al., 2008). Measurements of the gas concentrations (O_3, NO, NO_x, SO_2, CO) were carried out by using commercial analysers. All the trace gas instruments were maintained and calibrated routinely and the measurements are reported with uncertainties of 1 %. Meanwhile, an automatic meteorology station was operated to obtain meteorology parameters including temperature, relative humidity, pressure and radiation.

All the observed data are averaged to 10 min in order to be consistent with the particle number size distribution measurements. The measured parameters and instrumentation used in this study are listed in Table 1.

2.2 Model description

2.2.1 MALTE

For model simulations we used the zero-dimensional version of MALTE. The model structure is described in detail by Boy et al. (2006, 2008) and Lauros et al. (2011). MALTE includes modules for canopy emission of organic compounds, gas phase chemical reactions as well as aerosol physics. The emission module was disabled during our simulations, and instead the VOC concentrations obtained from PTR-MS measurements (e.g. methanol, acetaldehyde, acetone, isoprene, methyl vinyl ketone (MVK) and methyl acrolein (MACR), methyl ethyl ketone (MEK), benzene, toluene, styrene, aromatic compounds including 8 and 9 carbon atoms respectively and monoterpenes) were used as input. Simultaneously GC-MS-FID measurements were used to estimate the separation of compounds with the same m/z (MVK and MACR, the C8 aromatic compounds, the C9 aromatic compounds, and the monoterpenes). In addition, the atmospheric trace gases SO_2, NO, NO_x, CO, O_3 and the measured condensation sink (CS) for sulfuric acid were likewise used as input to the model.

2.2.2 Chemistry

Organic and inorganic chemical reactions were mostly selected from the MCM v3.2 (Saunders et al., 2003; Jenkin et al., 2003) via web site: http://mcm.leeds.ac.uk/MCM/. Meanwhile, additional reactions from Atkinson (1994) and Atkinson et al. (2004) were also included. The chemical equations (differential equations and compound concentrations) are calculated by the Kinetic PreProcessor (KPP) (Damian et al., 2002). The complete MCM reaction paths for methane, formaldehyde, methanol, acetaldehyde, acetone, isoprene, MVK, MACR, MEK, 2-methyl-3-buten-2-ol (MBO), alpha-pinene and beta-pinene were included. Likewise, the full chemistry paths for the following aromatic compounds were included: benzene, toluene, styrene and the following C8-aromatic compounds: ethylbenzene, o-xylene and m-xylene, as well as the following C9-aromatic compounds: propylbenzene, 1-ethyl-2-methyl benzene, 1-ethyl-3-methyl benzene, 1-ethyl-4-methyl benzene, 1,3,5-trimethyl benzene and 1,2,4-trimethyl benzene. In addition, the first order reactions between OH, O_3, NO_3 and the following compounds: cineole, ocimene, sabinene, camphene, myrcene, delta-3-carene, limonene,“other monoterpenes” than those mentioned here, beta-caryophyllene, farnesene, and “other sesquiterpenes” than those mentioned here, were also included. Acetonitrile was also measured, but not included in the model simulations, due to unknown chemistry. Totally the chemistry included 2293 chemical species and 6604 reactions. Relevant research with more detailed description for the chemistry modelling part has been published by Mogensen et al. (2011).

2.2.3 Aerosol

Particle number size distribution patterns are estimated by the UHMA model, which is responsible for the aerosol dynamic simulation in MALTE. All the basic aerosol dynamic processes including nucleation, condensation, coagulation and dry deposition are implemented in the model (Korhonen et al., 2004). The UHMA model has been successful in predicting the new particle formation observed in forest and coastal environments (Vuollekoski et al., 2009; Boy et al., 2006). In the present study we use the fixed sectional approach with 36 size bins. The size of the critical cluster is set to 1.5 nm in the model according to field observations (Kulmala et al., 2007) and quantum chemical calculations (Zhang, 2010).

Both the activation ($J = A[H_2SO_4]$) and kinetic nucleation ($J = K[H_2SO_4]^2$) theories proposed in the ambient studies are first tested in the model. A and K refer to the activation and kinetic nucleation coefficients, respectively, with values of $3 \times 10^{-6}\,s^{-1}$ and $8 \times 10^{-13}\,m^3\,s^{-1}$. These values are close to the measured median values of 17 NPF event days during CAREBeijing 2008 (Wang et al., 2013). Recent research results indicate that sulfuric acid is not the only compound taking part in new particle formation, but low-volatile organic vapours are also needed (Metzger et al., 2010; Kerminen et al., 2010; Riipinen et al., 2012; Lauros et al., 2011). Here the homogenous heteromolecular nucleation mechanism, sulfuric acid-organic nucleation ($J = K_{het}[H_2SO_4][Org]$), is also tested in the model. However, the specific organic species involved in the nucleation process are still unclear. Therefore, following the previous studies (Laaksonen et al., 2008; Paasonen et al., 2010; Lauros et al., 2011), we assume that the organic vapours are the products of alpha-pinene and beta-pinene via OH radicals oxidation (MTOP). The nucleation coefficient K_{het} is chosen as $3.0 \pm 3.4 \times 10^{-12}\,m^3\,s^{-1}$. This value is two to three orders of magnitude higher than that in previous model simculations (Lauros et al., 2011), laboratory experiments (Metzger et al., 2010) as well as field studies (Paasonen et al., 2010).

The subsequent growth of newly formed particles is a crucial secondary transformation process. Both sulfuric acid and the oxidation products of organic components by reactions with OH are assumed as the condensing vapours according to the nano-Köhler theory (Kulmala et al., 2004a). In addition, water, sulfuric acid and reaction products of organic components, oxidized by OH, NO_3 and O_3, participate in the conventional condensational growth of particles. For our model simulations, we have defined the condensing vapours as the first stable oxidation products for reactions between OH, O_3, NO_3 and all the organic compounds for which we have included the full chemistry path. Since no saturation vapour pressure estimation is currently included in our model, we have assumed that 0.5 % of the concentration of the compounds that we have classified as being condensing vapours, actually condense onto the particles. This value is one order of magnitude lower compared with previous study by Lauros et al. (2011), however, it leads to a good agreement with the observed growth rates. Moreover, we should keep in mind that in a polluted area like urban Beijing, probably a lot of other VOCs beside the ones we measured will contribute to the particle growth. For this reason, the factor had to be decreased to a much lower value in this study.

Besides the gaseous species concentrations, meteorological parameters (temperature, relative humidity, pressure and radiation), photolysis rates (J_{O^1D} and J_{NO_2}) as well as the initial particle number size distribution are also used as input variables. In total, 12 days with complete observation data, including 4 non-event days and 8 new particle formation event days are investigated. The simulation time period is the entire day from 00:00 to 24:00. The integrate time in the model is 10 s and the output data are averaged to 10 min in order to compare with the observation results.

3 Results and discussion

3.1 The simulation of sulfuric acid concentration

The condensation sink which describes how rapidly vapour molecules can condense onto the pre-existing particles, is used to represent the sink term of sulfuric acid in the model. The CS values can be directly obtained from the measured particle number size distributions, and expressed as (Kulmala et al., 2001):

$$\mathrm{CS} = 2\pi D \sum \beta D_p N \quad (2)$$

Here, D is the diffusion coefficient of the condensing vapour, β is the transitional regime correction factor, D_p is the aerosol particle diameter and N is their number concentration. In addition, the particle number size distributions are calculated at ambient relative humidity, while the hygroscopic growth is achieved by using the parameterization of Massling et al. (2009) based on the measurement results in Beijing.

Figure 1 displays the measured and simulated sulfuric acid concentrations for four selected days including one non-event day (day 219) and three nucleation event days (day 228, day 244 and day 256). The mean condensation sink (during 08:00–11:00) on a non-event day ($CS = 0.079\,s^{-1}$) is typically significantly higher than that on the three NPF event days, with mean values of $0.006\,s^{-1}$, $0.014\,s^{-1}$ and $0.038\,s^{-1}$, respectively, representing clean, median polluted and polluted situations. In general, the significant increase of the sulfuric acid concentration is observed from 08:00 with the peak shown at noon. A clear diurnal cycle of the modelled sulfuric acid concentration agrees to a large extent with the measurements (slope = 0.72 during the daytime). The correlation coefficients between the observed and modelled sulfuric acid concentrations are 0.78 (morning) and 0.81 (afternoon) for the total 12 investigated cases (see Table 2), respectively. The maximum midday sulfuric acid concentrations vary between 3.1×10^6 and $1.1 \times 10^7\,cm^{-3}$ for the observations (all investigated day), corresponding to 1.2×10^6 to $1.0 \times 10^7\,cm^{-3}$ for the modelled results. The ratios of peak values between the observed and modelled concentrations are within a factor of 3, with a median value of 1.3 ± 0.6.

In MALTE, the sulfuric acid concentrations are underestimated compared with the observations, especially during the morning rush hours. The modelled sulfuric acid concentrations only account for 62 % of the observations (Table 2). One possible explanation is that we potentially underestimate the nitrous acid (HONO) concentration in the model (HONO was not measured). A previous study (Kurtenbach et al., 2001) pointed out that traffic emissions can produce considerable HONO concentrations. Meanwhile, the photolysis of HONO is proved to be a significant source of the OH radical, especially in the early morning (Su et al., 2008). Therefore, the lack of measured HONO concentrations in the model might lead to the underestimation of sulfuric acid concentrations, especially at the urban site with heavy traffic emissions.

Best agreement between the modelled and observed sulfuric acid concentrations happened in the afternoon (during 12:00–18:00), with the slope of 0.88. Overall, the modelled results correlate well with the measured data points during the daytime (R = 0.74) compared with that during the nighttime (R = 0.53). This phenomenon is due to the lack of understanding of the nighttime chemistry. However, considering the NPF event has not been observed during the nighttime, the missing sulfuric acid in the nighttime will not be discussed further in this study.

In MALTE, the underestimation of sulfuric acid concentrations, by up to a factor of two compared with the measurement, were also found in other sites such as Hyytiälä and Hohenpeissenberg (Boy et al., 2012). Several other potential routes to produce sulfuric acid in the ambient atmosphere have been proposed recently. The evidence from computational studies, field observations and laboratory experiments all show that organic compounds such as Criegee Intermediates or their derivatives have significant capacity to oxidise SO_2 into SO_3 rapidly, which might lead to an enhancement of gaseous sulfuric acid yields in the ambient atmosphere (Kurteìn et al., 2011; Mauldin III et al., 2012; Boy et al., 2012; Berndt et al., 2012). Moreover, the SO_2 oxidation involving electron excited oxygen molecules could denote an additional source of sulfuric acid under specific condition (Sorokin, 2010). However, these theories have not been applied in the box model-version used at present, which might cause the underestimation of the modelled sulfuric acid concentration.

3.2 The simulation of new particle formation

6 August (Day 219) and 12 September (Day 256) are selected as examples of a non-event day and a NPF event day, respectively. The diurnal variations of particle number size distributions from the measurement and model simulation with two proposed nucleation mechanisms are presented in Fig. 2. The modelled on- and offset of new particle formation as well as the starting time of the NPF event are in good agreement with observations. The time shifts of the starting time of the NPF event between observation and simulation are achieved within half an hour in 6 NPF cases (in total 8 cases). An

obvious underestimation of the particle number concentration in the Aitken mode is observed in the model compared with the measurements. This might attributed to the fact that the local traffic emissions are not completely included in the box model. Hence, following the previous study (Wang et al., 2011), the particle number concentration in the size range 3–6 nm ($N_{3\text{–}6}$) is selected to represent the newly formed particles in this study, as shown in Fig. 3. The slight fluctuations of $N_{3\text{–}6}$ from the simulation at noon are still observed even on the non-event day (Figs. 2c, 2e and 3a). However, the maximum value is only 700 cm^{-3}, which is much lower than that on NPF event days. A better agreement between the observed and modelled $N_{3\text{–}6}$ on 12 September is found when the nucleation process is assumed as kinetic-type (See Fig. 3b). Although the increase of the simulated $N_{3\text{–}6}$ is 20 min earlier than that of the observation, the maximum value is 8000 cm^{-3} which is close to the ambient measurement (9000 cm^{-3}). The peak of simulated $N_{3\text{–}6}$ values is only 2900 cm^{-3} on 12 September when activation nucleation is assumed. This result is expected because the specific activation nucleation coefficient achieved from the observed particle nucleation rates and sulfuric acid concentrations is $6 \times 10^{-6}\,\text{s}^{-1}$ on 12 September (Wang et al., 2011), which is twice as high compared with the value used in the model (median value of 17 NPF event days). Totally, the statistical results suggest that the model overestimates the number concentrations of newly formed particles on 4 non-event days and underestimate them on 8 NPF event days. On average, the ratios between the observed and modelled maximum $N_{3\text{–}6}$ values in activation and kinetic nucleation types are 0.8 ± 0.4 and 0.7 ± 0.5 on non-event days, respectively. On the contrary, the ratios are 2.2 ± 1.4 and 1.5 ± 1.3 on NPF event days.

Moreover, Fig. 4 displays the measured and modelled particle number size distributions using kinetic nucleation and homogenous heteromolecular nucleation theories. MALTE could predict the occurrence of new particle formation with the nucleation mechanism involving the organic vapours (Fig. 4c). In the model, the ultrafine particle mode is formed around 10:20 in the morning, which is close to the ambient measurement (10:10). The diurnal variations of number concentrations of newly formed particles are exhibited in Fig. 5. The maximum value of the modelled $N_{3\text{–}6}$ with homogenous heteromolecular nucleation is 8000 cm^{-3}, which is the same as the modelled $N_{3\text{–}6}$ with kinetic nucleation and close to the ambient measurement (9000 cm^{-3}). However, the significant time delay (about two hours) is shown between the model simulations and measurements. Therefore, the specific organic species possibly involved in the atmospheric nucleation are still unknown in the polluted urban environment of Beijing. More information on the nucleation process and chemical compositions of freshly formed particles is needed.

4 Summary

The box model version of MALTE, including gas phase chemical reactions as well as aerosol physics and dynamics, was applied to predict the sulfuric acid concentration as well as the new particle formation in the polluted urban environment of Beijing, China. The chemical processes and aerosol dynamics were calculated by using MCM v3.2 and the UHMA code, respectively. Totally, 12 selected days (8 with new particle formation events and 4 without) with complete measurement data were investigated in this study.

The best agreement (slope = 0.88, $R = 0.81$) between the measured and modelled sulfuric acid concentrations was seen in the afternoon (during 12:00–18:00). The sulfuric acid concentrations are significantly underestimated in the model compared with the measurements, especially during the morning rush hours and nighttime. This result indicates that unknown important production pathways of the OH radical or SO_2 oxidation mechanisms are missing in the model, which might further lead to the underestimation of the sulfuric acid concentration. Although we have not included the recently proposed production paths for sulfuric acid into MALTE, the simulated sulfuric acid concentrations are acceptable during the daytime.

Classic nucleation mechanisms including activation nucleation and kinetic nucleation were tested in the UHMA model. The nucleation coefficients ($3 \times 10^{-6}\,\mathrm{s}^{-1}$ and

$8 \times 10^{-13}\,m^3\,s^{-1}$) were determined based on the 17 new particle formation events observed during the CAREBeijing 2008 campaign. The model was able to predict the occurrence of new particle formation under these two tested nucleation theories. The diurnal maximum number concentration of newly formed particles ($N_{3–6}$) calculated based on the kinetic nucleation mechanism seems more reasonable, comparing with the activation nucleation. However, on average, it is still 1.5 times higher than that in ambient measurements for all investigated NPF event cases. Totally, the statistical results suggest that the model overestimates $N_{3–6}$ on non-event days and underestimates them on NPF event days.

Moreover, homogenous heteromolecular nucleation ($J = K_{het}[H_2SO_4][Org]$) was also tested in this study. The organic vapours involved in the nucleation process are assumed to be the oxidation products of monoterpenes by OH radical. The diurnal patterns of particle number size distributions as well as the number concentrations of newly formed particles were close to the observation. However, a significant time delay of the number concentration peak is observed, implying that the specific organic components involved in the nucleation process still should be concerned in the further research.

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Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Table 1. Atmospheric parameters and instrumentation from the CAREBeijing 2008 campaign that are used in this study.

Parameters	Instruments	Ref.
Particle number size distribution	TDMPS, IfT	Wehner et al. (2008)
Sulfuric acid	ID-CIMS, TA&MU	Zheng et al. (2011)
VOCs	PTR-MS, Ionicon Analytik	Yuan et al. (2010)
J_{O^1D}/J_{NO_2}	Filter Radiometer, METCON Inc.	Bohn et al. (2008)
$SO_2/NO/NO_x/CO/O_3$	Gas analyzers, Ecotech Inc.	–
Pressure/Temperature/ Relative humidity/Radiation	M7115, LSI LASTEM s.r.l	–

Table 2. Comparisons of the modelled and measured sulfuric acid concentrations during different time period for 12 investigated days. Slope represents the ratio between the modelled and observed sulfuric acid concentrations.

Time period	Slope	Correlation coefficient (*R*)
Morning (6:00–12:00)	0.62	0.78
Afternoon (12:00–18:00)	0.88	0.81
Daytime (6:00–18:00)	0.72	0.74
Nighttime (00:00–6:00 and 18:00–24:00)	0.32	0.53

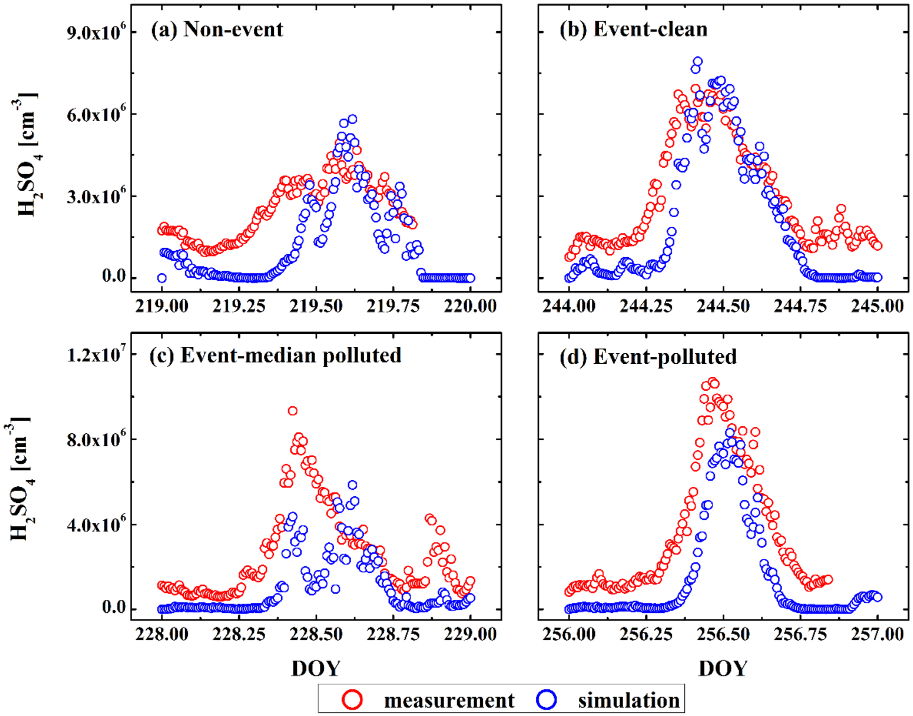

Fig. 1. Measured (red) and modelled (blue) sulfuric acid concentrations for four selected days in diverse pollution condition. **(a)** Non-event day, **(b–d)** NPF event days. The x-axis is presented by DOY (day of year).

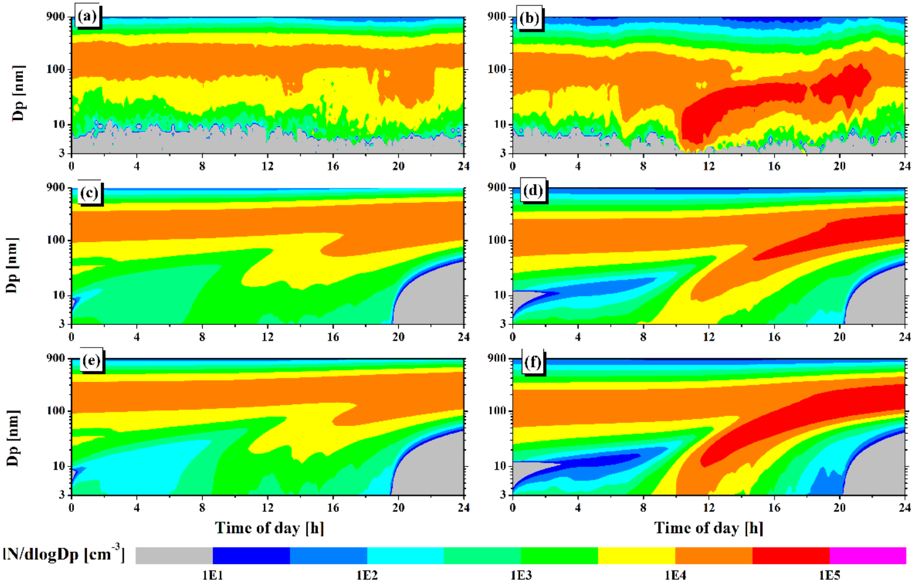

Fig. 2. Measured and modelled particle number size distributions for two selected days. Left panel represents the example of non-event day (6 August, day 219), right panel represents the example of a NPF event day (12 September, day 256); **(a)** and **(b)** measurement, **(c)** and **(d)** modelled with activation nucleation mechanism, **(e)** and **(f)** modelled with kinetic nucleation mechanism.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀|
|▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

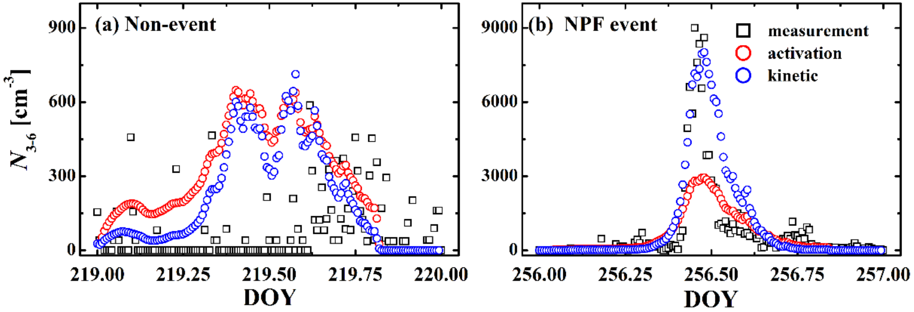

Fig. 3. Measured and modelled particle number concentrations in the size range 3–6 nm (N_{3-6}) for two selected days. **(a)** a non-event day (6 August, day 219), **(b)** NPF event day (12 September, day 256); black square: measurement, red circle: modelled with activation nucleation mechanism, blue circle: modelled with kinetic nucleation mechanism.

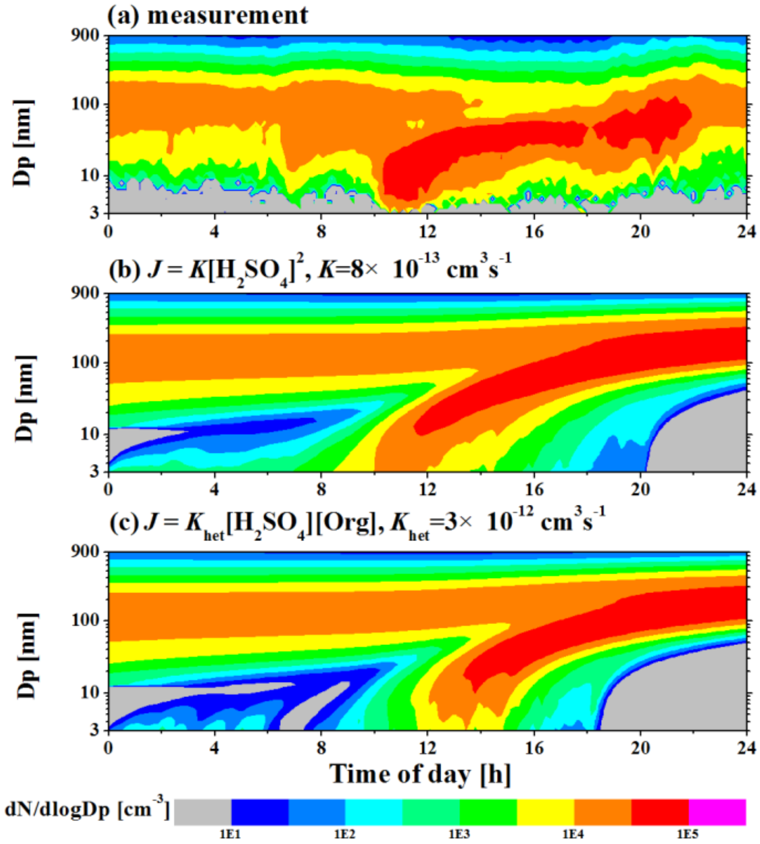

Fig. 4. Measured and modelled particle number size distributions on 12 September. **(a)** measurement; **(b)** modelled with kinetic nucleation mechanism; **(c)** modelled with homogenous heteromolecular kinetic nucleation mechanism.

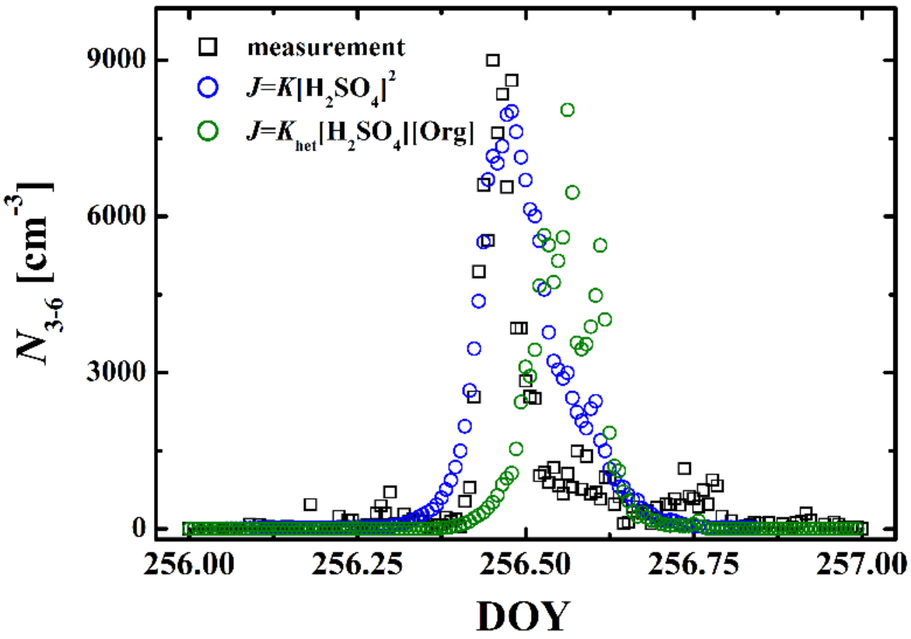

Fig. 5. Measured and modelled particle number concentrations in the size range 3–6 nm (N_{3-6}) on 12 September. Black square: measurement, blue circle: modelled with kinetic nucleation mechanism, green circle: modelled with homogenous heteromolecular kinetic nucleation mechanism.