Atmos. Chem. Phys. Discuss., 12, 11415–11443, 2012
www.atmos-chem-phys-discuss.net/12/11415/2012/
doi:10.5194/acpd-12-11415-2012

Atmospheric Chemistry and Physics Discussions

Particle hygroscopicity during atmospheric new particle formation events: implications for the chemical species contributing to particle growth

Z. Wu, W. Birmili, L. Poulain, M. Merkel, B. Fahlbusch, D. van Pinxteren, H. Herrmann, and A. Wiedensohler

Leibniz Institute for Tropospheric Research, Permoserstraße 15, 04318 Leipzig, Germany

Received: 11 April 2012 – Accepted: 18 April 2012 – Published: 3 May 2012

Correspondence to: Z. Wu (wuzhijun@tropos.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

This study examines the hygroscopicity of newly formed particles (smaller than 50 nm in particle mobility diameter) during two atmospheric new particle formation events with and without clear growth process at mid-level mountain range in Central Germany based on HCCT field campaign. Particle hygroscopicity measurements show that the particle soluble fractions at the end of event for two events are, respectively 60 % (45 nm particles for the event with clear growth) and 20 % (30 nm particles for the event without clear growth), stressing that non-soluble organic compounds may play a key role in particle growth during new particle formation event. Such significant difference in particle hygroscopicity also suggests that the chemical species responsible for nucleation particle growth are considerably different between the two selected NPF events. During both events, the hygroscopicity of newly formed particles decreased with particle growth, indicating that more less-hygroscopic compounds contribute to the subsequent condensation in contrast to the earlier stage. Sulfuric acid was considered to be responsible of the NPF event and represent the highly hygroscopic compounds. However, calculation demonstrated that sulfuric acid condensation failed to fully explain the observed soluble fraction in the nucleation mode particles. Therefore, we hypothesize that some water-soluble matters may explain the missing soluble fraction.

1 Introduction

New particle formation (NPF) from gaseous precursors has been observed in almost any part of the earth's atmosphere (Kulmala et al., 2004b). NPF is an important source of atmospheric particles and likely contributes to the balance of optically active particles (Kulmala et al., 2011), and cloud condensation nuclei (Spracklen et al., 2008; Wiedensohler et al., 2009; Wang and Penner, 2009; Laaksonen et al., 2005; Yue et al., 2011). NPF has thus the potential to influence climatologically important processes such as precipitation patterns and Earth's energy balance (IPCC, 2007). However, the mechanisms of atmospheric nucleation and particle subsequent growth still remain unclear. Sulfuric acid is the main species thought to be responsible for atmospheric NPF (Brus et al., 2011; Kulmala et al., 2006; Sipilä et al., 2010). Recently, sufficient evidences showed that organics also play important roles in atmospheric NPF processes (e.g., Zhang et al., 2004b; Kiendler-Scharr et al., 2009; Wang et al., 2010; Ristovski et al., 2010).

To quantitatively understand the NPF and subsequent growth process, it is critical to obtain information on the chemical species involved. Recently, a novelty instrument, thermal desorption chemical ionization mass spectrometry, was developed and used to measure the particle chemical composition of sub-20 nm during NPF events (Smith et al., 2004, 2005, 2010; Barsanti et al., 2009). Due to the tiny particle masses involved, the direct determination of chemical composition of newly formed particles is still a tedious task. Alternatively, measurements of particle volatility and/or hygroscopicity have been referred to provide indirect information on the chemical species contributing to particle growth (Väkevä et al., 2002; Sakurai et al., 2005; Wehner et al., 2005; Ehn et al., 2007; Petäjä et al., 2007; Asmi et al., 2010; Ristovski et al., 2010; Modini et al., 2009).

Both sulfuric acid and organic compounds were found to contribute to the subsequent particle growth after nucleation (e.g., Smith et al., 2004; Yue et al., 2010; Pierce et al., 2011; Ehn et al., 2007; Kulmala et al., 2004a). Their relative fraction in the particle phase seems to depend on the type of atmospheric environment (e.g., Boy et al., 2005; Yue et al., 2010; Stolzenburg et al., 2005). In the polluted atmosphere of Atlanta, USA, the available amount of sulfuric acid was sufficient to explain all of the observed particle growth (Stolzenburg et al., 2005), however, sulfuric acid represents only 30 % of the newly formed particles in the rural atmosphere of Hohenpeissenberg, Southern Germany (Birmili et al., 2003), and only around 10 % in the boreal forest area of Finland (Boy et al., 2005).

Due to the differences in hygroscopicity of sulfuric acid and/or its ammonium salts and secondary organics (Virkkula et al., 1999; Varutbangkul et al., 2006; Tang and

Munkelwitz, 1994), the hygroscopic measurements during NPF events can give insight into the changes in condensing vapor properties during NPF events and chemical composition of newly formed particles (Hämeri et al., 2001; Ehn et al., 2007; Ristovski et al., 2010). In Hyytiälä, Finland, the solubility of the mode of new particles decreased as the modal diameter increased from 10 to 50 nm during NPF events, indicating that the vapors responsible for particle growth changed (Ehn et al., 2007). They also observed that the hygroscopicity of 10 nm particles significantly varied with different events and stressed that the mechanism producing these particles is different.

In this study, we investigated the particle number size distributions and particle hygroscopic growth at a mid-level mountain site in Germany during the field experiment Hill Cap Cloud Thuringia 2010 (HCCT-2010). Two NPF events with different features could be characterized in much detail. Based on the hygroscopicity measurements of the nucleation mode and additional numerical calculations, the possibilities of various chemical species contributing to the detected growth of the nucleation mode are evaluated.

2 Experiments

2.1 Measurement site

The measurements of the entire campaign HCCT-2010 were performed in September and October 2010 in the Thüringer Wald mid-level mountain range in Central Germany. The main objective of HCCT-2010 was to perform a ground-based Langrangian-type experiment for investigating the influences of clouds on aerosol chemistry. During the campaign, three research stations were employed: Schmücke (the summit of the mountain, 937 m a.s.l.), Goldlauter (upwind site, 605 m a.s.l.), and Gehlberg (downwind site, 732 m a.s.l.). The air distance between Goldlauter and Schmücke stations is about 3 km. A more detailed description about the sampling sites can be found in Herrmann et al. (2005). In this paper, we will refer to measurements at Goldlauter only, i.e. where particle hygroscopicity and aerosol mass spectroscopic measurements were concurrently made.

2.2 Particle hygroscopicity measurements

The hygroscopicity measurements were conducted at Goldlauter research station. The particle hygroscopicity is investigated using a hygroscopicity tandem differential mobility particle analyzer (H-TDMA). The H-TDMA used in this study has been illustrated in previous publications in detailed (Massling et al., 2003, 2007; Wu et al., 2011), and complies to the instrumental standards prescribed in Massling et al. (2011). The experiments were conducted in a temperature-controlled container (20 °C). The relative humidity (RH) of the sampling air was kept to below 30 % using an automatic silica gel dryer system.

The hygroscopic growth factor (HGF) is defined as the ratio of the particle mobility diameter, $D(\mathrm{RH})$, at a given RH to the dry diameter, D_d:

$$\mathrm{HGF}(\mathrm{RH}) = \frac{D(\mathrm{RH})}{D_\mathrm{d}} \tag{1}$$

The data inversion is based on the TDMAinv method developed by Gysel et al. (2009). Dry scans (under RH < 10 %) are used to calibrate any offset between DMA1 and DMA2 and define the width of the HTDMA's transfer function (Gysel et al., 2009). In this study, the HGFs at RH = 90 % were measured.

2.3 Other useful parameters

Other measured parameters used in the data analysis and corresponding instruments are given in Table 1. To estimate the concentration of sulfuric acid, we referred to the global radiation data measured at Schmücke rather than Goldlauter because the mountain shadow blocked the sunlight in the morning at Goldlauter.

Back trajectories arriving at the sampling site were calculated using the NOAA "HYSPLIT-4" trajectory model (Draxier and Hess, 1998). The 72-h trajectories terminated on a height of 800 m above ground at 08:00, 10:00, 12:00, 14:00, 16:00 and 18:00 local time (UTC+01) will be used in further analysis.

2.4 Derivation of the soluble particle fraction

Based on the Zdanovskii–Stokes–Robinson (ZSR) method (Zdanovskii, 1948; Stokes and Robinson, 1966), the hygroscopic growth factor of a mixture can be estimated from the HGF_i of the pure components and their respective volume fractions, ε_i (Malm and Kreidenweis, 1997):

$$\mathrm{HGF}_{\mathrm{mixed}} = \left(\sum_i \varepsilon_i \mathrm{HGF}_i^3\right)^{1/3} \tag{2}$$

Here, we assume that two components including soluble and insoluble fractions contribute to the particle growth (also refer to Ehn et al., 2007; Swietlicki et al., 1999). Then, ε of soluble fraction can be calculated by:

$$\varepsilon_{\mathrm{soluble}} = \frac{\mathrm{HGF}^3_{\mathrm{measured}} - 1}{\mathrm{HGF}^3_{(\mathrm{NH_4})_2\mathrm{SO_4}} - 1} \tag{3}$$

The soluble fraction is assumed as ammonium sulfate, and the insoluble fraction is secondary organics, which are typically hydrophobic. The growth factors of $(NH_4)_2SO_4$ in different diameters were calculated according to the water activity reported by Tang and Munkelwitz (1994).

The assumption of insoluble organic fraction may lead to overestimate the soluble fraction because atmospherically relevant secondary organics typically have a growth factor larger than 1 (e.g., Varutbangkul et al., 2006). This implies that in the presence of several classes of hygroscopic substances, ε derived from Eq. (3) is only an "equivalent" soluble fraction (i.e. assuming ammonium sulfate as the only soluble substance). ε derived from Eq. (3) is therefore an upper estimate for the true soluble volume fraction.

2.5 Estimation of H_2SO_4 concentration

The concentration of sulfuric acid is estimated according to the proximity measure reported by Mikkonen et al. (2011):

$$[\mathrm{H_2SO_4}] = 8.21 \times 10^{-3} \cdot k \cdot \mathrm{Radiation} \cdot [\mathrm{SO_2}]^{0.62} (\mathrm{CS} \cdot \mathrm{RH})^{-0.13} \tag{4}$$

where $k = 0.85$ at 12 °C is the reaction rate constant, which is calculated according to the Eq. (3) in Mikkonen et al. (2011) and is scaled by multiplying it with 10^{12}. CS is the condensation sink, which determines how rapidly molecules will condense onto pre-existing aerosols (Kulmala et al., 2005). CS in s^{-1} is calculated according to Dal Maso et al. (2005) under dry condition. Radiation is global radiation in $\mathrm{W\,m^{-2}}$, RH is relative humidity in %. SO_2 is the concentration of sulfur dioxide in molecules $\mathrm{cm^{-3}}$. This method is constructed for data where the radiation is greater than $10\,\mathrm{W\,m^{-2}}$ but the predictive ability is significantly better when the radiation is greater than $50\,\mathrm{W\,m^{-2}}$ (Mikkonen et al., 2011). As shown in Fig. 1, during new particle formation events, the radiation is strong enough to ensure that the proxy is accurate.

2.6 Estimation of particle growth

The evolution of the number size distribution of nucleation mode over time in the ambient can be well characterized by an evolving lognormal distribution (Stolzenburg et al., 2005; Lee et al., 1984, 1990):

$$\frac{\mathrm{d}N}{\mathrm{d}\ln D_\mathrm{p}} = \frac{N}{\sqrt{2\pi Z}} \exp\left(-\frac{\ln^2 (D_\mathrm{p}/D_\mathrm{g})}{2Z}\right) \tag{5}$$

where D_p is particle diameter, N and D_g, are, respectively total particle number concentration and geometric number mean particle diameter (GMD). Here $Z = \ln^2 \sigma_\mathrm{g}$, and σ_g is geometric number standard deviation of the mode.

The observed growth rate ($\mathrm{GR_{obs}}$) can be calculated using the following equation over a certain time period:

$$\mathrm{GR_{obs}} = \frac{\mathrm{d}D_g}{\mathrm{d}t} \tag{6}$$

Theoretically, the growth process can be broken down into three mechanisms including intramodal coagulation (Coag_I), extramodal coagulation (Coag_E) with larger particles and vapor condensation (Cond.). The modal growth rates contributed by these three mechanisms can be obtained by solving the time derivative of the first moment (M_k, $k = 1$) in particle volume of nucleation mode where

$$M_k(t) = \int_{\mathrm{mode}} v^k n(v,t)\,\mathrm{d}\ln v = N(t)\cdot D_g^{3k}(t)\cdot \exp\left[\frac{9}{2}k^2 Z(t)\right] \tag{7}$$

$$n(v,t) = \frac{\mathrm{d}N}{\mathrm{d}\ln v} = \frac{1}{3}\frac{\mathrm{d}N}{\mathrm{d}\ln D_\mathrm{p}} \tag{8}$$

$$v = \frac{\pi D_\mathrm{p}^3}{6} \tag{9}$$

Details of these calculations can be found in Stolzenburg et al. (2005). H_2SO_4 is assumed to be the condensing vapor responsible for the particle growth. Later, the sulfuric acid present on the particles is neutralized by up-take of gas phase ammonia. The condensation rate is limited by the mass transfer rate of H_2SO_4 molecules onto the nucleation mode particles.

The growth rate of particle volume contributing by H_2SO_4 condensation and subsequent NH_3 neutralization can be estimated with the assumption of spherical particle:

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{\mathrm{d}\left(\frac{\pi}{6}D_\mathrm{g}^3\right)}{\mathrm{d}t} = \frac{\pi}{2}D_\mathrm{g}^2\mathrm{GR} \tag{10}$$

$$v_\mathrm{t} = v_0 + \frac{\mathrm{d}v}{\mathrm{d}t} \times \Delta t \tag{11}$$

where $\mathrm{GR} = \mathrm{d}D_\mathrm{g}/\mathrm{d}t$ is condensational growth rate, v_t is the particle volume at time t assuming that only H_2SO_4 condensation contribute to particle growth. v_0 is the original particle volume at time 0. The $\mathrm{d}v/\mathrm{d}t$ is the average of volume growth rate during a given time period. At this point, we assumed that the original particle only consists of ammonium sulfate. Then, the volume fraction of $(NH_4)_2SO_4$ in total particle volume (V_t), $\varepsilon_{(NH_4)_2SO_4}$, can be estimated as:

$$\varepsilon_{(\mathrm{NH_4})_2\mathrm{SO_4}} = \frac{v_t}{V_t} = \frac{v_t}{\pi \cdot D_{\mathrm{g},t}^3/6} \tag{12}$$

$D_{\mathrm{g},t}$ is the D_g derived from Eq. (5) at time t. Here, assuming original particle as ammonium sulfate may not cause larger error due to the tiny mass compared to the particles after growing. In addition, we assume that the particle intramodal coagulation can also contribute to sulfate fraction in particles. Therefore, the GR used in Eq. (10) includes both H_2SO_4 condensation and intramodal coagulation growth.

3 Results

3.1 New particle formation events

Two NPF events were observed on 12 and 14 October 2010. The temporal evolution of the particle number size distribution and the meteorological parameters is shown in

Fig. 1. On 12 October, the event started at noon, i.e. at a time when temperature was rapidly increasing, and RH decreasing. During this event, northerly winds prevailed at wind speeds below $2\,\mathrm{m\,s^{-1}}$. The wind direction measured in the summit station also showed that north wind is the prevailing wind during this time period. As shown in Fig. 2a, no changes in the pathway of air mass arriving at the sampling site were observed on 12 October. The NPF event lasted several hours and ended around 20:00 when the wind speed increased significantly. Meanwhile, the event showed a classical clear growth process.

The second event occurred on 14 October started at 11:00 also in associating with a decreasing RH and an increasing temperature. At 14:00, the event was interrupted when the wind direction switched from south to north. Afterwards, a burst in nucleation mode with relatively larger particles was observed. They showed no significant growth until the event ended at around 18:00. On 14 October, the backward trajectories show that the air mass significantly changed at noon, as shown in Fig. 2b. After 14:00, the air parcels spent less time over continental areas in contrast to those before 14:00. This may bring clean air, which contains less condensable vapors.

As shown in Fig. 3 the burst in 10–25 nm particle number concentration was not accompanied by a SO_2 spike, thus confirming that the newly formed particles were not produced inside a plume of any nearby source. In addition, the events with similar features were observed at all research stations (summit, downwind, and upwind sites, plots are given in Supplement, Fig. S1), indicating that the event has a spatial extension. Both NPF events occurred when the calculated H_2SO_4 concentration was relatively high. This is consistent with the previous studies showing that sulfuric acid plays an important role in atmospheric nucleation and early growth (e.g., Birmili et al., 2003; Zhang et al., 2004a; Kulmala et al., 2004b). During NPF event on 12 October, mean NH_3 and O_3 concentrations are $0.7\,\mu\mathrm{g\,m^{-3}}$ and 16.5 ppb, respectively. Differently, a much lower NH_3 concentration ($0.09\,\mu\mathrm{g\,m^{-3}}$) and higher O_3 concentration (28.0 ppb) were observed, as shown in Fig. 3.

3.2 Particle hygroscopicity during NPF events

As shown in Fig. 4, the GMD of nucleation mode grew from 10 nm up to 40 nm on 12 October. HGFs of 30, 35, 40, and 45 nm particles during the NPF event were measured by HTDMA. A significant change in GMD was not observed on 14 October because the event was prematurely cut off due to an air mass change (see Fig. 2b). On 14 October, HGFs of 25 and 30 nm particles were measured. The results are shown in the upper panel of Fig. 4. On 12 October, the HGFs ranged between 1.4 and 1.55, which is much higher than those on 14 October (HGFs = 1.2–1.35). The HGFs showed a deceasing trend during the course of the event. This phenomenon was observed for both events and is independent of particle size.

As shown in Fig. 4 (a2), the soluble equivalent fraction of nucleation mode particles was between 0.6 and 0.7 on 12 October, implying that the co-condensation of H_2SO_4 and NH_3 can plausibly account for a substantial volume fraction of the particles. Organic vapors are likely to account for the rest of the particle growth. The inverted HTDMA data showed a perfect single hygroscopicity mode (see Fig. S2 in supplementary material). This means that the nucleation mode particles were internally well-mixed. During the subsequent particle growth, the soluble fraction decreased. Such a decrease in particle solubility along with modal diameter growth was also observed in previous experiments in Finland (e.g., Ehn et al., 2007; Kulmala et al., 2001). Based on our observation, we hypothesize that less hygroscopic condensable vapors may play a key role during the advanced stage of nucleation mode growth.

On 14 October, the soluble fraction accounts for 30 % of 25 nm particles at 15:30. In comparison with 12 October, this can be interpreted that organic condensable vapors contributed more to the particle growth at smaller nucleation mode particle sizes or that organic species took even part in nucleation (Zhang et al., 2004b). On 14 October, no obvious particle growth could be observed as a result of the air mass change, whereas the soluble fraction of 30 nm particle decreased to 20 % at the end of event. One possible reason is chemical reactions occurred in the particle phase and produced less hydrophilic compounds. Recently, laboratory experiments gave evidences that organic vapors (2,4-hexadienal, glyoxal and trimethylamine) enhance the growth of H_2SO_4 nanoparticles by producing oligomers, polymers and alkylaminium sulfates in the particle phase (Wang et al., 2010). In comparison with ammonium sulfate and sulfuric acid, these compounds have lower hygroscopicity. Another possible reason is more hydrophobic compounds condensed on particles and make particle grow, whereas, the transport and dilution of spatially inhomogeneous aerosols may cause no obvious growth in nucleation mode.

3.3 Discussion of the chemical species contributing to particle growth

In order to quantify condensational growth of sulfuric acid, the growth rate is calculated using the method shown in Sect. 2.6. The calculated growth rate reported in Table 2 is the average of the growth rate during the given time period. On 12 October between 12:00 and 17:00, the mean growth rate due to sulfuric acid condensation is $0.28\,\mathrm{nm\,h^{-1}}$, which only accounts for around 6 % of the observed growth rate. By considering the intra-modal and extra-modal coagulation growth, the total calculated growth rate is $1.09\,\mathrm{nm\,h^{-1}}$, which is much lower than the observed growth rate. After ruling out H_2SO_4 condensation and NH_3 neutralization and coagulation as sources of particle growth, low volatile organics may be potential contributors to the remaining growth rate.

The fraction of $(NH_4)_2SO_4$ in particle total volume at 17:00 on 12 October was estimated according to the Eq. (12) by considering H_2SO_4 condensation and subsequent NH_3 neutralization and intramodal coagulation. The result shows that $(NH_4)_2SO_4$ can only explain 18 % of particle volume when the particles grew from 10 nm to 40 nm. However, the soluble fraction estimated in the Sect. 3.2 is around 66 % of particle volume at 17:00 (see Fig. 4a2). As mentioned above, the atmospheric secondary organics may contribute to the particle growth. These secondary organics, however, which are typically considered as less hygroscopic compounds, cannot explain the rest of soluble fraction. This may indicate that some other soluble chemical compounds contributing to the particle growth. There are two possibilities. First, ammonium nitrate, which is very soluble compound, may contribute to the particle growth under low temperature (refer to Fig. 1). Second, amines in forming organic salts were proposed to be a pathway for contributing to atmospheric nanoparticle growth (Smith et al., 2010; Barsanti et al., 2009). Laboratory measurements of alkylammonium–carboxylate salt nanoparticles showed only slightly lower hygroscopicity than ammonium sulfate nanoparticles (Smith et al., 2010). Recently, Smith and coworkers (2010) have shown that alkylammoniumcarboxylate salts account for 20–50 % of the mass of freshly nucleated particles in locations that include Atlanta, Mexico City, Boulder, and Hyytiälä, while sulfates account for only about 10 %. That new finding may partly explain the missing source of soluble fraction.

During the event on 14 October, no gradual growing process was observed. Therefore, the observed growth rate cannot be calculated using Eq. (6). The mean H_2SO_4 concentration is 6.9×10^6 molecule cm^{-3}. Correspondingly, the estimated growth rate is 0.36 nm h^{-1}. By taking coagulation growth into account, the total growth rate is 1.17 nm h^{-1}. This means that H_2SO_4 condensation and coagulation growth can fully explain the slight change in particle size of nucleation mode. This may cause an increase in particle hygroscopicity. However, the HTDMA measurements show an inverse pattern with decreasing soluble fraction. This observation reinforced that the condensation of organic vapor or chemical reactions in the particulate phase may play a key role in the evolvement of newly formed particles during this event.

The nucleation mode particles cannot be detected by AMS. Nevertheless, the AMS data can provide supportive information to analyze the chemical composition of newly formed particles (e.g., Zhang et al., 2004a, 2011). The time series of particle chemical composition and their share in PM_1 (particulate matter with diameter below 1 µm) during events are presented in Fig. 5. On 12 October, both sulfate and organics concentrations during the first three-hours of the event increased obvious. Later, the sulfate concentration continued to enhance until event is ended. The distinctive growth of sulfate fraction during NPF event was also observed by Zhang et al. (2004a) in the urban atmosphere. The chemical composition share in the lower panel of Fig. 5 shows that sulfate fraction increased step-wisely, while the organic fraction declined. Differently, on 14 October, both sulfate and organic concentrations decreased during the first hour of event. Afterwards, they increased until the end of event. And, no significant change in the share of sulfate was observed during the whole event period. The difference in temporal variation of sulfate fraction in PM_1 may give a clue that H_2SO_4 play a more important role in the particle formation and post growth on 12 October in contrast to 14 October 2010.

The ion molar ratio ($\text{Ratio} = [NH_4^+/18]/([NO_3^-/62] + 2 \cdot [SO_4^{2-}/96] + [Cl^-/35.5])$ of measured ammonium concentrations to the measured sulfate and nitrate is calculated to examine the particle acidity (Zhang et al., 2007). The results are presented in Fig. 5. The ion molar ratios on 12 and 14 October are, respectively 0.93 and 0.90, which are close to 1, indicating that sulfate and nitrate are almost neutralized in the form of ammonium nitrate and ammonium sulfate. However, looking into detail on the time dependency of the ion molar ratio, an increasing in the ratio can be systematically observed during each NPF period. In the beginning of NPF event, the increase in PM_1 acidity was observed for both cases and may be interpreted as addition of sulfuric acid and/or ammonium bisulfate on pre-existing particles, indicating that there is in rich of acidic substance in the atmosphere during this time period. This may imply that non-neutralized compounds contribute to the NPF process in earlier stage of the event. Then, the ratio shows an increasing trend with particle growing. Zhang et al. (2004a) also observed that ammonium was present at very low concentrations during the initial stages of the new particle formation event. This observation suggests that condensed H_2SO_4 may be neutralized by NH_3 gradually with particle growing.

4 Conclusions

The particle hygroscopic growth of nucleation mode was investigated to analyze the chemical species contributing to particle growth during NPF events at a mid-level mountain range, Thüringer Wald, in Central Germany. Two cases with and without clear growth process are analyzed in this study. A significant difference in particle hygroscopicity was observed between the two NPF events, indicating that the chemical species driving particle growing were not exactly the same. During both events, the hygroscopic growth of newly formed particles decreased with particle growing. Apparently, the chemical nature of the condensing vapors changed during the particle growth process from more to less hygroscopic species.

An analysis of AMS data confirmed that sulfate may have played a more pronounced role in the first NPF case featuring a clear growth process. The contribution of sulfuric acid condensation to the soluble fraction was estimated. Result shows that a larger soluble fraction fails to be explained by H_2SO_4 condensation, indicating that some other water-soluble compounds contribute to the particle growth. In earlier stage of NPF event, higher PM_1 acidity provides a clue that non-neutralized compound, most likely H_2SO_4 contribute to the particle growth in the beginning of event. Then, these non-neutralized compounds are neutralized by NH_3 gradually with particle growing.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/11415/2012/acpd-12-11415-2012-supplement.pdf.

References

Asmi, E., Frey, A., Virkkula, A., Ehn, M., Manninen, H. E., Timonen, H., Tolonen-Kivimäk, O., Aurela, M., Hillamo, R., and Kulmala, M.: Hygroscopicity and chemical composition of antarctic sub-micrometre aerosol particles and observations of new particle formation, Atmos. Chem. Phys., 10, 4253–4271, doi:10.5194/acp-10-4253-2010, 2010.

Barsanti, K. C., McMurry, P. H., and Smith, J. N.: The potential contribution of organic salts to new particle growth, Atmos. Chem. Phys., 9, 2949–2957, doi:10.5194/acp-9-2949-2009, 2009.

Birmili, W., Berresheim, H., Plass-Dülmer, C., Elste, T., Gilge, S., Wiedensohler, A., and Uhrner, U.: The hohenpeissenberg aerosol formation experiment (hafex): a long-term study including size-resolved aerosol, H_2SO_4, OH, and monoterpenes measurements, Atmos. Chem. Phys., 3, 361–376, doi:10.5194/acp-3-361-2003, 2003.

Boy, M., Kulmala, M., Ruuskanen, T. M., Pihlatie, M., Reissell, A., Aalto, P. P., Keronen, P., Dal Maso, M., Hellen, H., Hakola, H., Jansson, R., Hanke, M., and Arnold, F.: Sulphuric acid closure and contribution to nucleation mode particle growth, Atmos. Chem. Phys., 5, 863–878, doi:10.5194/acp-5-863-2005, 2005.

ten Brink, H., Otjes, R., Jongejan, P., and Slanina, S.: An instrument for semi-continuous monitoring of the size-distribution of nitrate, ammonium, sulphate and chloride in aerosol, Atmos. Environ., 41, 2768–2779, doi:10.1016/j.atmosenv.2006.11.041, 2007.

Brus, D., Neitola, K., Hyvärinen, A. P., Petäjä, T., Vanhanen, J., Sipilä, M., Paasonen, P., Kulmala, M., and Lihavainen, H.: Homogenous nucleation of sulfuric acid and water at close to atmospherically relevant conditions, Atmos. Chem. Phys., 11, 5277–5287, doi:10.5194/acp-11-5277-2011, 2011.

Dal Maso, M., Kulmala, M., Riipinen, I., Wagner, R., Hussein T., Aalto, P. P., and Lehtinen, A. K. E. J.: Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland, Boreal Environ. Res., 10, 323–336, 2005.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal. Chem., 78, 8281–8289, doi:10.1021/ac061249n, 2006.

Draxier, R. R. and Hess, G. D.: An overview of the HYSPLIT_4 modelling system for trajectories, dispersion and deposition, Aust. Meteorol. Mag., 47, 295–308, 1998.

Ehn, M., Petäjä, T., Aufmhoff, H., Aalto, P., Hämeri, K., Arnold, F., Laaksonen, A., and Kulmala, M.: Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid, Atmos. Chem. Phys., 7, 211–222, doi:10.5194/acp-7-211-2007, 2007.

Gysel, M., McFiggans, G. B., and Coe, H.: Inversion of tandem differential mobility analyser (TDMA) measurements, J. Aerosol Sci., 40, 134–151, 2009.

Hämeri, K., Väkevä, M., Aalto, P. P., Kulmala, M., Swietlicki, E., Zhou, J., Seidl, W., Becker, E., and O'Dowd, C. D.: Hygroscopic and ccn properties of aerosol particles in boreal forests, Tellus B, 53, 359–379, doi:10.1034/j.1600-0889.2001.530404.x, 2001.

Herrmann, H., Wolke, R., Müller, K., Brüggemann, E., Gnauk, T., Barzaghi, P., Mertes, S., Lehmann, K., Massling, A., Birmili, W., Wiedensohler, A., Wieprecht, W., Acker, K., Jaeschke, W., Kramberger, H., Svrcina, B., Bächmann, K., Collett Jr, J. L., Galgon, D., Schwirn, K., Nowak, A., van Pinxteren, D., Plewka, A., Chemnitzer, R., Rüd, C., Hofmann, D., Tilgner, A., Diehl, K., Heinold, B., Hinneburg, D., Knoth, O., Sehili, A. M., Simmel, M., Wurzler, S., Majdik, Z., Mauersberger, G., and Müller, F.: Febuko and modmep: field measurements and modelling of aerosol and cloud multiphase processes, Atmos. Environ., 39, 4169–4183, doi:10.1016/j.atmosenv.2005.02.004, 2005.

Kiendler-Scharr, A., Wildt, J., Maso, M. D., Hohaus, T., Kleist, E., Mentel, T. F., Tillmann, R., Uerlings, R., Schurr, U., and Wahner, A.: New particle formation in forests inhibited by isoprene emissions, Nature, 461, 381–384, 2009.

Kulmala, M., Maso, M. D., MäKelä, J. M., Pirjola, L., VäKevä, M., Aalto, P., Miikkulainen, P., Hämeri, K., and O'Dowd, C. D.: On the formation, growth and composition of nucleation mode particles, Tellus B, 53, 479–490, doi:10.1034/j.1600-0889.2001.530411.x, 2001.

Kulmala, M., Laakso, L., Lehtinen, K. E. J., Riipinen, I., Dal Maso, M., Anttila, T., Kerminen, V. M., Hõrrak, U., Vana, M., and Tammet, H.: Initial steps of aerosol growth, Atmos. Chem. Phys., 4, 2553–2560, doi:10.5194/acp-4-2553-2004, 2004a.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, doi:10.1016/j.jaerosci.2003.10, 2004b.

Kulmala, M., Petäjä, T., Mönkkönen, P., Koponen, I. K., Dal Maso, M., Aalto, P. P., Lehtinen, K. E. J., and Kerminen, V. M.: On the growth of nucleation mode particles: source rates of condensable vapor in polluted and clean environments, Atmos. Chem. Phys., 5, 409–416, doi:10.5194/acp-5-409-2005, 2005.

Kulmala, M., Lehtinen, K. E. J., and Laaksonen, A.: Cluster activation theory as an explanation of the linear dependence between formation rate of 3nm particles and sulphuric acid concentration, Atmos. Chem. Phys., 6, 787–793, doi:10.5194/acp-6-787-2006, 2006.

Kulmala, M., Arola, A., Nieminen, T., Riuttanen, L., Sogacheva, L., de Leeuw, G., Kerminen, V. M., and Lehtinen, K. E. J.: The first estimates of global nucleation mode aerosol concentrations based on satellite measurements, Atmos. Chem. Phys., 11, 10791–10801, doi:10.5194/acp-11-10791-2011, 2011.

Laaksonen, A., Hamed, A., Joutsensaari, J., Hiltunen, L., Cavalli, F., Junkermann, W., Asmi, A., Fuzzi, S., and Facchini, M. C.: Cloud condensation nucleus production from nucleation events at a highly polluted region, Geophys. Res. Lett., 32, L06812, doi:10.1029/2004gl022092, 2005.

Lee, K. W., Chen, J., and Gieseke, J. A.: Log-normally preserving size distribution for brownian coagulation in the free-molecule regime, Aerosol Sci. Technol., 3, 53–62, doi:10.1080/02786828408958993, 1984.

Lee, K. W., Curtis, L. A., and Chen, H.: An analytic solution to free molecule aerosol coagulation, Aerosol Sci. Technol., 12, 457–462, doi:10.1080/02786829008959360, 1990.

Malm, W. C. and Kreidenweis, S. M.: The effects of models of aerosol hygroscopicity on the apportionment of extinction, Atmos. Environ., 31, 1965–1976, doi:10.1016/s1352-2310(96)00355-x, 1997.

Maßling, A., Wiedensohler, A., Busch, B., Neusüß, C., Quinn, P., Bates, T., and Covert, D.: Hygroscopic properties of different aerosol types over the Atlantic and Indian Oceans, Atmos. Chem. Phys., 3, 1377–1397, doi:10.5194/acp-3-1377-2003, 2003.

Massling, A., Leinert, S., Wiedensohler, A., and Covert, D.: Hygroscopic growth of sub-micrometer and one-micrometer aerosol particles measured during ACE-Asia, Atmos. Chem. Phys., 7, 3249–3259, doi:10.5194/acp-7-3249-2007, 2007.

Massling, A., Niedermeier, N., Hennig, T., Fors, E. O., Swietlicki, E., Ehn, M., Hämeri, K., Villani, P., Laj, P., Good, N., McFiggans, G., and Wiedensohler, A.: Results and recommendations from an intercomparison of six Hygroscopicity-TDMA systems, Atmos. Meas. Tech., 4, 485–497, doi:10.5194/amt-4-485-2011, 2011.

Mikkonen, S., Romakkaniemi, S., Smith, J. N., Korhonen, H., Petäjä, T., Plass-Duelmer, C., Boy, M., McMurry, P. H., Lehtinen, K. E. J., Joutsensaari, J., Hamed, A., Mauldin III, R. L., Birmili, W., Spindler, G., Arnold, F., Kulmala, M., and Laaksonen, A.: A statistical proxy for sulphuric acid concentration, Atmos. Chem. Phys., 11, 11319–11334, doi:10.5194/acp-11-11319-2011, 2011.

Modini, R. L., Ristovski, Z. D., Johnson, G. R., He, C., Surawski, N., Morawska, L., Suni, T., and Kulmala, M.: New particle formation and growth at a remote, sub-tropical coastal location, Atmos. Chem. Phys., 9, 7607–7621, doi:10.5194/acp-9-7607-2009, 2009.

Petäjä, T., Kerminen, V. M., Dal Maso, M., Junninen, H., Koponen, I. K., Hussein, T., Aalto, P. P., Andronopoulos, S., Robin, D., Hämeri, K., Bartzis, J. G., and Kulmala, M.: Sub-micron atmospheric aerosols in the surroundings of marseille and athens: physical characterization and new particle formation, Atmos. Chem. Phys., 7, 2705–2720, doi:10.5194/acp-7-2705-2007, 2007.

Pierce, J. R., Riipinen, I., Kulmala, M., Ehn, M., Petäjä, T., Junninen, H., Worsnop, D. R., and Donahue, N. M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, Atmos. Chem. Phys., 11, 9019–9036, doi:10.5194/acp-11-9019-2011, 2011.

Ristovski, Z. D., Suni, T., Kulmala, M., Boy, M., Meyer, N. K., Duplissy, J., Turnipseed, A., Morawska, L., and Baltensperger, U.: The role of sulphates and organic vapours in growth of newly formed particles in a eucalypt forest, Atmos. Chem. Phys., 10, 2919–2926, doi:10.5194/acp-10-2919-2010, 2010.

Sakurai, H., Fink, M. A., McMurry, P. H., Mauldin, L., Moore, K. F., Smith, J. N., and Eisele, F. L.: Hygroscopicity and volatility of 4–10 nm particles during summertime atmospheric nucleation events in urban atlanta, J. Geophys. Res., 110, D22S04, doi:10.1029/2005jd005918, 2005.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, R. L., Hyvärinen, A.-P., Lihavainen, H., and Kulmala, M.: The role of sulfuric acid in atmospheric nucleation, Science, 327, 1243–1246, 2010.

Smith, J. N., Moore, K. F., McMurry, P. H., and Eisele, F. L.: Atmospheric measurements of sub-20 nm diameter particle chemical composition by thermal desorption chemical ionization mass spectrometry, Aerosol Sci. Technol., 38, 100–110, doi:10.1080/02786820490249036, 2004.

Smith, J. N., Moore, K. F., Eisele, F. L., Voisin, D., Ghimire, A. K., Sakurai, H., and McMurry, P. H.: Chemical composition of atmospheric nanoparticles during nucleation events in atlanta, J. Geophys. Res., 110, D22S03, doi:10.1029/2005jd005912, 2005.

Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and and McMurry, P. H.: Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, P. Natl. Acad. Sci. USA, 107, 6634–6639, 2010.

Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Sihto, S.-L., Riipinen, I., Merikanto, J., Mann, G. W., Chipperfield, M. P., Wiedensohler, A., Birmili, W., and Lihavainen, H.: Contribution of particle formation to global cloud condensation nuclei concentrations, Geophys. Res. Lett., 35, L06808, doi:10.1029/2007gl033038, 2008.

Stokes, R. H. and Robinson, R. A.: Interactions in aqueous nonelectrolyte solutions. I. Solute-solvent equilibria, J. Phys. Chem., 70, 2126–2130, 1966.

Stolzenburg, M. R., McMurry, P. H., Sakurai, H., Smith, J. N., Mauldin III, R. L., Eisele, F. L., and Clement, C. F.: Growth rates of freshly nucleated atmospheric particles in atlanta, J. Geophys. Res., 110, D22S05, doi:10.1029/2005jd005935, 2005.

Swietlicki, E., Zhou, J., Berg, O. H., Martinsson, B. G., Frank, G., Cederfelt, S. I., Dusek, U., Berner, A., Birmili, W., Wiedensohler, A., Yuskiewicz, B., and Bower, K. N.: A closure study of sub-micrometer aerosol particle hygroscopic behaviour, Atmos. Res., 50, 205–240, doi:10.1016/s0169-8095(98)00105-7, 1999.

Tang, I. N. and Munkelwitz, H. R.: Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance, J. Geophys. Res., 99, 18801–18808, doi:10.1029/94jd01345, 1994.

Väkevä, M., Kulmala, M., Stratmann, F., and Hämeri, K.: Field measurements of hygroscopic properties and state of mixing of nucleation mode particles, Atmos. Chem. Phys., 2, 55–66, doi:10.5194/acp-2-55-2002, 2002.

Varutbangkul, V., Brechtel, F. J., Bahreini, R., Ng, N. L., Keywood, M. D., Kroll, J. H., Flagan, R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Hygroscopicity of secondary organic aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds, Atmos. Chem. Phys., 6, 2367–2388, doi:10.5194/acp-6-2367-2006, 2006.

Virkkula, A., Van Dingenen, R., Raes, F., and Hjorth, J.: Hygroscopic properties of aerosol formed by oxidation of limonene, α-pinene, and β-pinene, J. Geophys. Res., 104, 3569–3579, doi:10.1029/1998jd100017, 1999.

Wang, L., Khalizov, A. F., Zheng, J., Xu, W., Ma, Y., Lal, V., and Zhang, R.: Atmospheric nanoparticles formed from heterogeneous reactions of organics, Nature Geosci., 3, 238–242, 2010.

Wang, M. and Penner, J. E.: Aerosol indirect forcing in a global model with particle nucleation, Atmos. Chem. Phys., 9, 239–260, doi:10.5194/acp-9-239-2009, 2009.

Wehner, B., Petäjä, T., Boy, M., Engler, C., Birmili, W., Tuch, T., Wiedensohler, A., and Kulmala, M.: The contribution of sulfuric acid and non-volatile compounds on the growth of freshly formed atmospheric aerosols, Geophys. Res. Lett., 32, L17810, doi:10.1029/2005gl023827, 2005.

Wiedensohler, A., Cheng, Y. F., Nowak, A., Wehner, B., Achtert, P., Berghof, M., Birmili, W., Wu, Z. J., Hu, M., Zhu, T., Takegawa, N., Kita, K., Kondo, Y., Lou, S. R., Hofzumahaus, A., Holland, F., Wahner, A., Gunthe, S. S., Rose, D., Su, H., and Pöschl, U.: Rapid aerosol particle growth and increase of cloud condensation nucleus activity by secondary aerosol formation and condensation: a case study for regional air pollution in Northeastern China, J. Geophys. Res., 114, D00G08, doi:10.1029/2008jd010884, 2009.

Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjäraa, A. M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J. A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Hüglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Gröning, C., Faloon, K., Beddows, D., Harrison, R., Monahan, C., Jennings, S. G., O'Dowd, C. D., Marinoni, A., Horn, H.-G., Keck, L., Jiang, J., Scheckman, J., McMurry, P. H., Deng, Z., Zhao, C. S., Moerman, M., Henzing, B., de Leeuw, G., Löschau, G., and Bastian, S.: Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions, Atmos. Meas. Tech., 5, 657–685, doi:10.5194/amt-5-657-2012, 2012.

Wu, Z. J., Nowak, A., Poulain, L., Herrmann, H., and Wiedensohler, A.: Hygroscopic behavior of atmospherically relevant water-soluble carboxylic salts and their influence on the water uptake of ammonium sulfate, Atmos. Chem. Phys., 11, 12617–12626, doi:10.5194/acp-11-12617-2011, 2011.

Yue, D. L., Hu, M., Zhang, R. Y., Wang, Z. B., Zheng, J., Wu, Z. J., Wiedensohler, A., He, L. Y., Huang, X. F., and Zhu, T.: The roles of sulfuric acid in new particle formation and growth in the mega-city of Beijing, Atmos. Chem. Phys., 10, 4953–4960, doi:10.5194/acp-10-4953-2010, 2010.

Yue, D. L., Hu, M., Zhang, R. Y., Wu, Z. J., Su, H., Wang, Z. B., Peng, J. F., He, L. Y., Huang, X. F., Gong, Y. G., and Wiedensohler, A.: Potential contribution of new particle formation to cloud condensation nuclei in beijing, Atmos. Environ., 45, 6070–6077, doi:10.1016/j.atmosenv.2011.07.037, 2011.

Zdanovskii, B.: Novyi metod rascheta rastvorimostei elektrolitov v mnogokomponentnykh sistema, Zh. Fiz. Khim+, 22, 1478–1485, 1486–1495, 1948.

Zhang, Q., Stanier, C. O., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Pandis, S. N., and Jimenez, J. L.: Insights into the chemistry of new particle formation and growth events in pittsburgh based on aerosol mass spectrometry, Environ. Sci. Technol., 38, 4797–4809, doi:10.1021/es035417u, 2004a.

Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T., and Molina, M. J.: Atmospheric new particle formation enhanced by organic acids, Science, 304, 1487–1490, doi:10.1126/science.1095139, 2004b.

Zhang, Q., Jimenez, J. L., Worsnop, D. R., and Canagaratna, M.: A case study of urban particle acidity and its influence on secondary organic aerosol, Environ. Sci. Technol., 41, 3213–3219, doi:10.1021/es061812j, 2007.

Zhang, Y. M., Zhang, X. Y., Sun, J. Y., Lin, W. L., Gong, S. L., Shen, X. J., and Yang, S.: Characterization of new particle and secondary aerosol formation during summertime in Beijing, China, Tellus B, 63, 382–394, doi:10.1111/j.1600-0889.2011.00533.x, 2011.

Table 1. Atmospheric parameters and instrumentation from the field experiment HCCT-2010 that are used in this study. All measurements were taken from the Goldlauter station except global radiation, which was taken from the Schmücke (summit) station.

Parameters	Instruments
Dry particle number size distribution (9–900 nm) (RH below 30 %)	Scanning Mobility Particle Sizer (SMPS) (Wiedensohler et al., 2010)
Particle chemical composition	High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) (DeCarlo et al., 2006)
NH_3	MARGA semi-continuous ambient air monitoring system (ten Brink et al., 2007)
SO_2 and O_3	TE 49C-TL O_3 monitor, TE43C-TL SO_2 monitor
Wind speed, wind direction, air temperature, and global radiation	Davis Vantage Pro2 weather station

Table 2. The observed and calculated growth rate.

Day Unit	Time Period	$[H_2SO_4]$ (cm^{-3})	GR_{obs} $nm\,h^{-1}$	Cond. $nm\,h^{-1}$	Coag_I $nm\,h^{-1}$	Coag_E $nm\,h^{-1}$	Sum $nm\,h^{-1}$
10/12	12:00–17:00	$5.0 \times 10^{+6}$	5.0	0.28	0.41	0.40	1.09
10/14	14:00–17:00	$6.9 \times 10^{+6}$	–	0.36	0.05	0.76	1.17

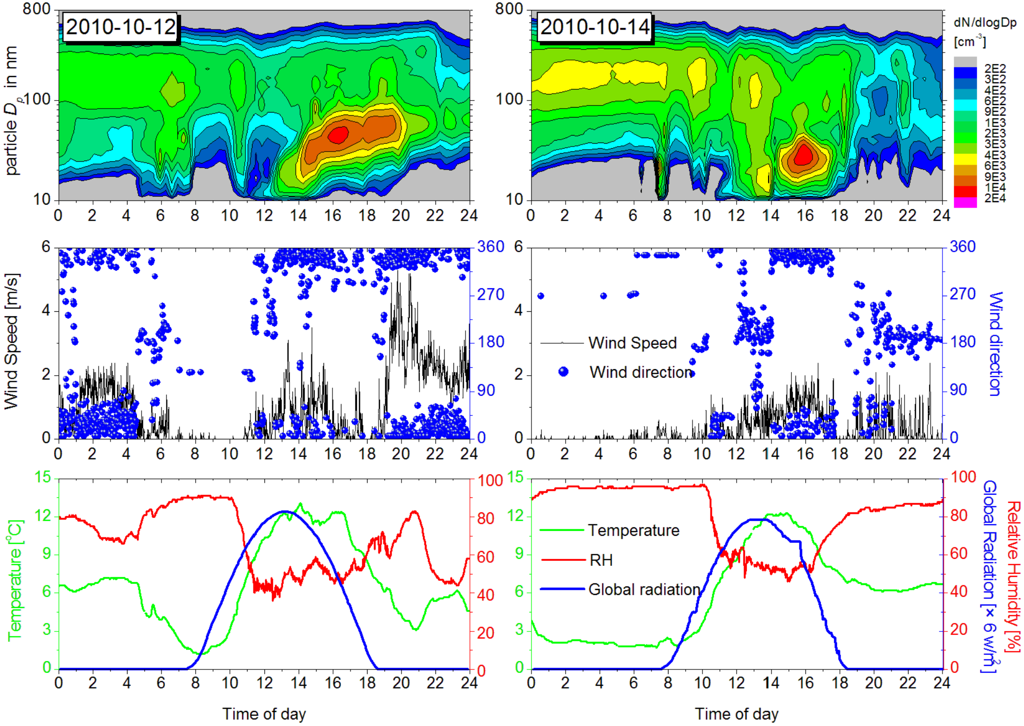

Fig. 1. The evolution of particle number size distribution and weather conditions on 12 and 14 October 2010.

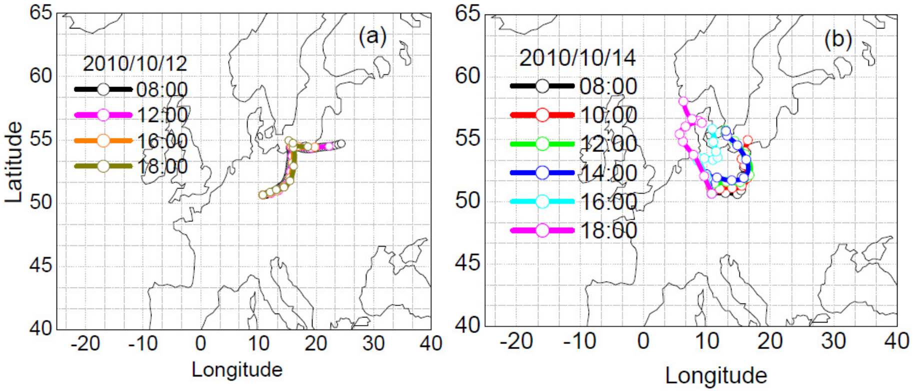

Fig. 2. 72-h backward trajectory of the air mass (800 m a.g.l.) arriving at the sampling site during NPF events.

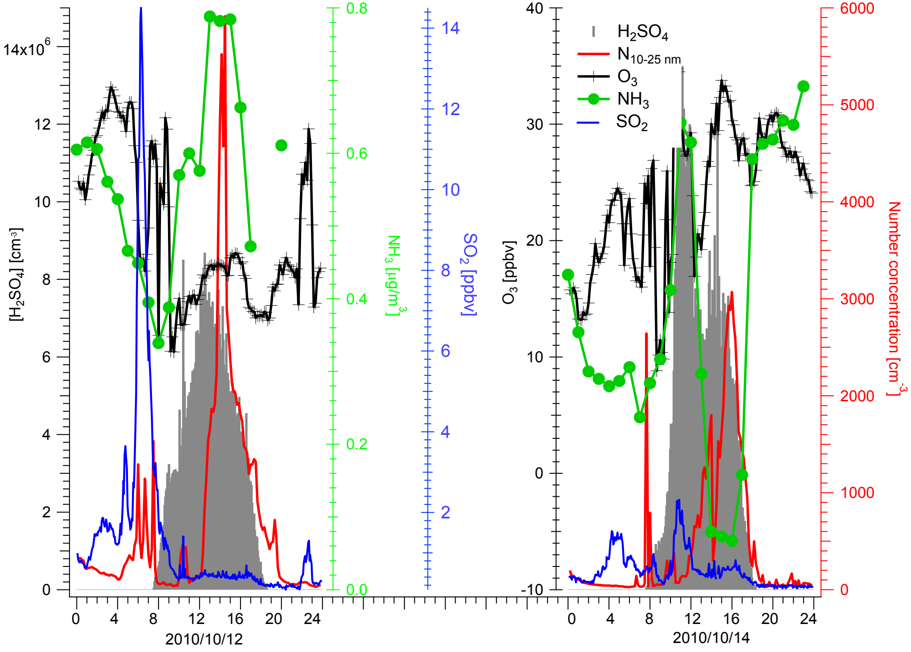

Fig. 3. Time series of trace gases concentration and particle number concentration of nuclei mode on NPF days.

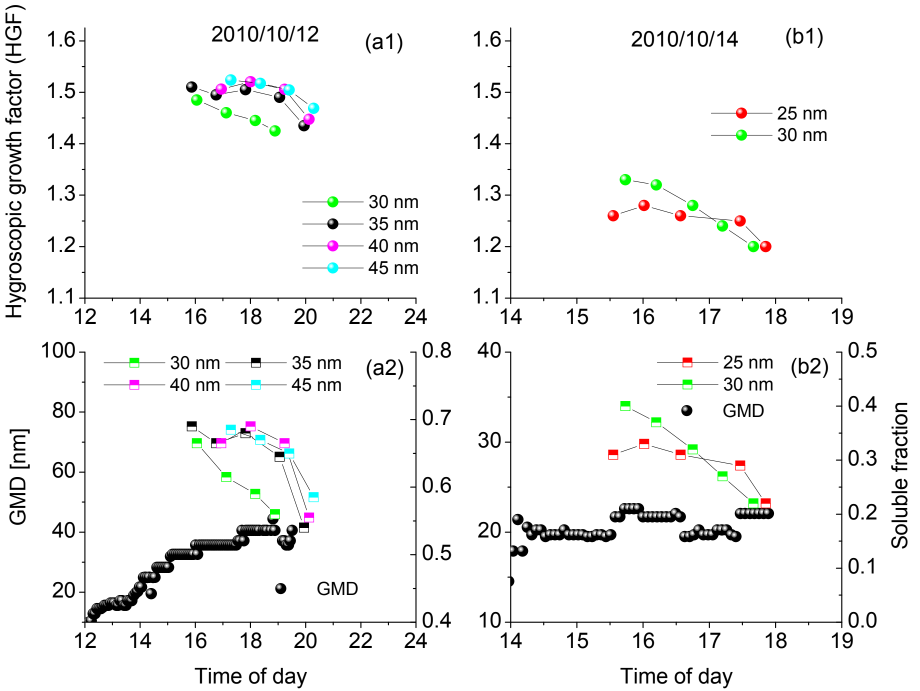

Fig. 4. The temporal evolution of GMD, HGF, and the soluble equivalent fraction during the two NPF events. Time is indicated in local time.

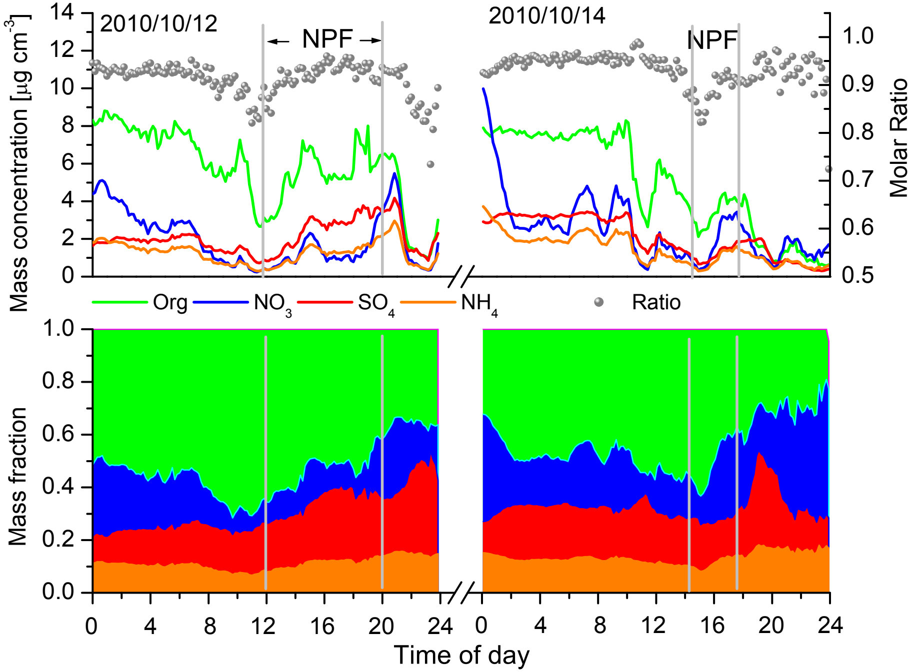

Fig. 5. Chemical composition and their share in PM$_1$ derived from AMS measurement on NPF days. The ion molar ratio is also shown in the figure.