

**Sulphates and
Organics in new
particle formation**

Z. D. Ristovski et al.

The role of sulphates and organic vapours in new particle formation in a eucalypt forest

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Abstract

The influence of biogenic particle formation on climate is a well recognized phenomenon. To understand the mechanisms underlying the biogenic particle formation, determining the chemical composition of the new particles and therefore the species that drive the particle production is of utmost importance. Due to the very small amount of mass involved, indirect approaches are frequently used to infer the composition. We present here the results of such an indirect approach by simultaneously measuring volatile and hygroscopic properties of newly formed particles in a forest environment. We that the particles are composed of both sulphates and organics, with the amount of sulphate component strongly depending on the available gas-phase sulphuric acid, and the organic components being photo-oxidation products of most likely a monoterpene. Our findings confirm a two-step process through nucleation and cluster formation followed by simultaneous growth by condensation of sulphates and organics that take the particles to climatically relevant sizes.

1 Introduction

The production of new aerosol particles from biogenic sources (forests, marine biota, etc) has been observed in a number of different environments (Kulmala et al., 2004). At regional scales, biogenic particle formation is a major source that determines the population of particles which seed droplet formation in clouds (cloud condensation nuclei (CCN)) (Tunved et al., 2006). This way, they influence cloud properties and thereby climate and the hydrological cycle (Kerminen et al., 2005). Determining the magnitude and drivers of biogenic aerosol production in different ecosystems is therefore crucial for the future development of climate models. Regardless of extensive research efforts, many aspects of biogenic particle production remain elusive. Most studies have been conducted in continental and coastal sites in the Northern Hemisphere (Kulmala et al., 2004). In the Northern European boreal region (Hyytiälä) studies of aerosol formation

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and transformation processes have been performed for many years. A picture of the main parameters influencing particle formation at this site is slowly emerging. The two major components of the freshly nucleated particles have been identified as sulphates and organics and their precursors are sulphuric acid and photo-oxidation products of volatile organic compounds (VOC's), respectively. Although sulphuric acid has been identified as one of the key components in aerosol formation and growth (Berndt et al., 2005; Riipinen et al., 2007), its exact role as well as the processes limiting new particle formation are still unclear. The presence of a large pool of neutral clusters has been recently experimentally observed (Kulmala et al., 2007b). It has been postulated that they are composed of ammonium bisulphate (Vehkamäki et al., 2004). The question that remains is up to what sizes these sulphate clusters can grow and what factors influence their growth. Measurements of the water uptake (hygroscopic growth) of freshly nucleated particles in the same environment (Ehn et al., 2007) indicate a large soluble component, most likely sulphates, in particles smaller than 20 nm. Although it seems that sulphates are responsible for the initial formation of particles they cannot explain their growth to observed sizes of over 50 nm (Boy et al., 2005). The vapours causing the condensational growth are low-vapour-pressure organic species whose exact chemical natures are unknown. Although there is relatively strong evidence that the growth rates and composition of larger than 50-nm particles are tied to the photo-oxidation of monoterpenes (Laaksonen et al., 2008; Tunved et al., 2006), evidence for the presence of these organic vapours in freshly nucleated 3–10 nm particles is scarce. This is mainly due to the lack of online analytical methods capable of assessing the composition of particles smaller than 30 nm in diameter. Until now, the main evidence has come from indirect methods that have measured the growth rates of newly formed particles when exposed to organic vapours (butanol (O'Dowd et al., 2002) and ethanol (Laaksonen et al., 2008)). Laaksonen et al. (2008) show evidence of a correlation between the gas-phase monoterpene oxidation product concentration and the growth rate of 10-nm particles in ethanol vapour. This correlation only exists during nucleation events. A similar approach has been used in the recently developed

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condensation particle counter battery (Kulmala et al., 2007a) where the composition of particles as small as 3 nm can be inferred through their activation properties in different vapours, namely butanol and water. Applying this technique at a rural background site (Hyytiälä), the authors show that the freshly formed particles at 3 and 11 nm contain water-soluble material. They further show (Riipinen et al., 2009) that at the smallest sizes (2–4 nm) the particles activate for growth at clearly smaller sizes in water than in butanol vapour, however less than would be expected from ammonium sulphate or sulphuric acid. This indicates a presence of other less hygroscopic components in freshly nucleated particles.

The main problem in developing online experimental techniques for the characterization of the chemical composition of freshly nucleated particles is the very low mass of the sample. However, indirect methods exist that are capable of shedding light into the composition of these particles. For instance, measurements of particle hygroscopic properties and/or volatility are often used to infer the composition of even the smallest particles below 20 nm (Johnson et al., 2005). Here we utilize a recently developed instrument, the Volatility and Hygroscopicity Tandem Differential Mobility Analyzer (VH-TDMA) (Johnson et al., 2004, 2008), that measures the volatility and hygroscopicity of particles simultaneously. The instrument selects a narrow particle size range from the ambient size distribution and heats the particles to a desired temperature. Any volatile material present in the particles will start to evaporate, which leads to a reduction in particle diameter. Next, the particles are exposed to a controlled high humidity. If the particle diameter increases (as a result of hygroscopic growth) a hydrophilic component must be present. The process is repeated several times so that with slowly increasing temperature, more of the particle is evaporated. This way, the particle diameter slowly decreases, and at regular intervals we then measure the hygroscopic growth of the remaining particle. The observed dependence of volatility and hygroscopic growth on temperature can then be compared with those of reference aerosols generated in the laboratory. Applying the above technique we show experimental evidence that, in a forest environment, the freshly nucleated particles consist of both sulphates and photo-

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oxidation products of a monoterpene, such as α -pinene. We also found the amount of sulphates present in particles to be closely related to the concentration of SO_2 , and therefore to sulphuric acid concentration (Boy et al., 2006). Furthermore, our results add to the increasing amount of evidence that oxidised monoterpenes are crucial for the subsequent condensational growth of the particles to climatically relevant sizes.

2 Materials and methods

2.1 Field measurements

The data collected in this work were measured in November 2006 as part of a larger measurement campaign EUCAP (Eucalypt Forest Aerosols and Precursors) at the Tumbarumba flux station ($35^\circ 39'20.6''$ S $148^\circ 09'7.5''$ E, 1200 m a.s.l.) in south eastern New South Wales, Australia. The Tumbarumba flux station is located in a tall open Eucalypt forest where the dominant species in this forest are *E. Delegatensis* (Alpine Ash) and *E. dalrympleana* (Mountain Gum) with average tree height of around 40 m. The instruments were located in a shed on the ground with the aerosol inlet at 2 m height. The size distribution of air ions was measured with an Air Ion Spectrometer (AIS; Airl LTD, Estonia) (0.34 to 40 nm) and the size distribution of the sum of neutral and charged airborne particles with a Scanning Mobility Particle Sizer (SMPS, TSI 3936) (5 to 168 nm). The combined volatile and hygroscopic properties of the particles were measured with a VH-TDMA. Both the SMPS and the AIS sampled continuously during the whole campaign with a time interval of 6 and 5 min between two samples, respectively. The AIS, capable of observing smaller particles (down to 0.34 nm) than the SMPS (5 nm in this study but usually down to 3 nm), is ideal for studying the initial steps of growth of new aerosol particles. In this study, the purpose of the AIS was to detect the new-particle formation events as early as possible so the VH-TDMA could be prepared for sampling the growing particles in time.

Once the nucleation event was observed and the newly formed particles reached

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a relatively stable size of 20–30 nm, this mode was selected and analysed by the VH-TDMA. The thermodenuder temperature was scanned from room temperature until the particles were completely volatilized or reduced in size below the detection range of the VH-TDMA (7.5 nm). The maximum thermodenuder temperature necessary for complete volatilisation ranged from 150 to 180°C, with a residence time of around 2 s. The particle volatilisation is presented through the volume fraction remaining $VFR=(D_v/D_{v0})^3$, where D_{v0} is the particle diameter at room temperature and D_v the particle diameter after heating in the thermodenuder to a temperature T_d . The change in the hygroscopic properties after volatilization is presented through the dependence of the hygroscopic growth factor $HGF=D_h/D_v$ on the thermodenuder temperature, where D_h is the particle diameter after volatilisation and subsequent humidification. For each thermodenuder temperature the VFR and the change in the HGF was measured. The relative humidity during temperature scans was kept constant at $RH=90\pm0.2\%$. The error bars for the HGF on all figures are $\pm2\%$ and come from the accuracy of particle sizing. SO_2 was measured by pulsed laser fluorescence (Thermo Environmental, Model 43C-TLE) from a height of 50 m. Sample air was drawn (13 Lpm) through a Teflon inlet line by a diaphragm pump. This flow was sub-sampled by the SO_2 analyzer along with other trace gas analyzers. Other trace gases measured from this inlet included O_3 (UV-absorption, Model 205, 2B Technology) and oxides of nitrogen (O_3 -induced chemiluminescence, Model 88Y, Ecophysics).

2.2 Chamber studies

Measurements of the volatile and hygroscopic properties of the photooxidation products of α -pinene were conducted in the smog chamber (Paulsen et al., 2005) at the Paul Scherrer Institute, Switzerland. Details of the experiments are presented in Meyer et al. (2009). The SOA was generated via photo-oxidation of α -pinene in a 27 m³ Teflon chamber at 20°C and 50% relative humidity. The chamber was first humidified to 50% RH before introducing NO_x . A known concentration of around 10 ppb of α -pinene (Fluka, 99.8%) was evaporated in a heated glass sampling bulb and con-

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tinuously flushed into the chamber with pure air. Four xenon arc lamps were used to simulate the solar light spectrum and initiate the photochemical reaction. The VH-TDMA measurements were conducted several hours since the lights were turned on and condensation of organic species was considered to have ceased.

3 Results and discussion

3.1 Observation of nucleation events

During the campaign, we observed new particle formation events almost on a daily basis. Figure 1 shows the particle size distribution measured with an SMPS (5–168 nm) during the nucleation events, while Fig. 2 shows the size distribution of air ions from 0.34 to 40 nm measured on the same days with the Air Ion Spectrometer. The particle formation events have started around noon and were preceded by relatively low particle concentrations. Especially strong nucleation events were observed on 8 and 10 November. It is interesting to observe that the highest SO₂ concentration was observed for the 10 November. From the above ion and particle size distributions, ion and particle growth rates in the range from 7–20 nm were calculated and are presented in Table 1. In addition the formation rate is also shown.

3.1.1 VH-TDMA measurements

Once the new particles had grown to a diameter of about 25 nm, we simultaneously measured their volatility and hygroscopicity as a function of the heating temperature (T_d) with the VH-TDMA. Figure 3a and b present the results for 9 and 10 November, respectively. When the particles are heated to about 50°C, the first volatile component starts to evaporate and VFR decreases abruptly (bottom graphs). As this component evaporates, HGF increases (top graphs). This indicates that the particles are composed of two components. The first component is more volatile but less hygroscopic

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while the second is less volatile but more hygroscopic. With increasing thermodynamic temperature, more and more of the first component evaporates leaving the more hygroscopic component within the particle. This results in further increase in the HGF.

However, the question remains, what are these two components? Organic compounds with low vapour pressure produced by photo-oxidation of monoterpenes are likely candidates for the first component. Indeed, in environments where monoterpenes are abundant, they have been identified as a major component of particle mass (Cavalli et al., 2006). They have relatively low HGF (Varutbangkul et al., 2006; Duplissy et al., 2008) and are volatile (Meyer et al., 2009). As further evidence that the first component is the product of photo-oxidation of a monoterpene such as α -pinene, Fig. 4 presents the volatilization of particles from a nucleation event observed on 9 November and from a photochemical chamber experiment with initial α -pinene concentration of 10 ppb (Meyer et al., 2009). These two curves show an excellent agreement which indicates that the more volatile but less hygroscopic particle component observed in the field measurements is of organic origin and the product of photo-oxidation of either α -pinene or some similar monoterpene.

We postulate that the second, more hygroscopic component is of a sulphate nature. Evidence for this comes from the distinct difference in both volatilisation and hygroscopic growth for the nucleation event observed on 10 November compared to those on 9 November. During this event, the observed HGF was significantly higher at room temperature than during the event on 9 November. The reason for this relates to the role that sulphates play in the new particle formation events. The maximum measured SO_2 concentration on 9 November did not exceed 200 pptv whereas on 10 November it reached approximately 800 pptv. From the condensational sink formed by pre-existing aerosol and from the concentrations of SO_2 , VOCs, CO, NO_x , and O_3 one can calculate the concentration of sulphuric acid molecules (Table 2) using a pseudo-steady state chemical box-model (Boy et al., 2005). This model was successfully verified against measured sulphuric acid data in Hyytiälä, Finland and incorporated all measurements from this campaign as input values. Taking the uncertainties from the measurements

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and the estimations for some not measured parameters, such as the RO_2 -radicals, an average uncertainty of 50% would be realistic. The concentration of sulphuric acid on 10 November was $15.3 \times 10^6 \text{ cm}^{-3}$, more than twice as high as the concentration on 9 November which was $7.3 \times 10^6 \text{ cm}^{-3}$. This increased concentration of sulphuric acid had led to a larger amount of sulphates present within the particles and, consequently, to the higher observed HGF.

A further question is whether the sulphate component was sulphuric acid or some other more neutralised form such as ammonium sulphate or bisulphate. Sulphuric acid is rather volatile and will start to evaporate from the particles at temperatures below 100°C . Since it is more hygroscopic than the photo-oxidation products of α -pinene, we should observe a reduction in HGF when it starts to evaporate, as we would be evaporating a more hygroscopic component. This should occur at thermodynamically temperatures above 100°C , however, contrary to this, our measurements showed an increase in HGF up to 140°C excluding sulphuric acid as the second component. Therefore, we postulate that the more hygroscopic component responsible for the initial particle growth was either ammonium sulphate or ammonium bisulphate, but not sulphuric acid. Both have similar HGF's and volatilisation curves as measured by our VH-TDMA (Johnson et al., 2004). This observation further points out to ammonium bisulphate as one of the candidates for neutral cluster formation in the atmosphere and its involvement in initial particle formation (Kulmala et al., 2007b).

Assuming that the two components are photo-oxidation products of organics (α -pinene) and ammonium sulphate, we fitted the measured HGF's to a theoretical model (see Appendix A). The only fitting parameter within the model is ϵ_0 , the initial volume fraction of sulphates within the particle. The fitted curves using the ZSR prediction are presented as full blue lines on Fig. 3 (top graphs) for the nucleation event observed on 9 and the 10 November. Associated uncertainties are taken into account for the error estimates of the ZSR predictions. The upper and lower confidence limits of the fitting procedure are presented as blue shaded regions. The values of the initial volume fraction of ammonium sulphate (ϵ_0) that was used as the fitting parameter are presented

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in Table 2 together with the calculated maximum concentrations of H_2SO_4 molecules.

The fitted curves are in good agreement with the experimental results. On 10 November (high SO_2 concentration) ϵ_0 was as high as 50% whereas on the 9th of November it was around 6%. Analyses of other events with similar concentrations of SO_2 as on 9 November led to similar values of ϵ_0 . At high thermodenuder temperatures (130°C and 150°C for the 10 and 9 November, respectively) the particles had reduced in size to 20 and 10 nm. Most of the organic component had evaporated and the particles consisted mainly of the sulphate component. A further increase in temperature led to the evaporation of the sulphate and the decrease of the measured HGF according to the Kelvin effect. This effect was more pronounced on 10 November as the sulphate fraction was much larger.

4 Conclusions

These results clearly show that the sulphate component present in the particles is not sulphuric acid but a more neutralized form, either ammonium sulphate or bisulphate. Our calculations further show that sulphates in most cases are responsible for a reasonably small fraction (<6%) of the growth (see Table 2) with the organics being responsible for the remaining fraction. The only exception was the day with very high SO_2 concentration where the sulphates were responsible for almost 50% of the growth. We further observed a particle growth rate, in the 7–20 nm range, that was almost independent of size (see Table 1). Thus our results actually confirm the existence of a two-step process suggested by Kulmala et al. (2000, 2007b) with nucleation and cluster formation and subsequent growth of these particles being carried out not only by one component but by simultaneous growth of sulphates and organics.

As the sulphates compromise only a small fraction of the total particle volume whether the particles will grow to climatically relevant sizes will depend on the available organic vapours, which in the forest environment, we have shown to be the gas-phase oxidation products of monoterpenes. There is no reason why these findings cannot be

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extended to other biogenic aerosol systems such as both coastal and remote marine environments. Indeed, photo-oxidation products of other secondary organic aerosol precursors, such as isoprene produced by phytoplankton, have been proposed as major contributors to the change in the size distribution of CCN in the Southern Ocean (Meskhidze and Nenes, 2006). Biogenic atmospheric particle formation is a global phenomenon and as such the observed role of sulphates together with organic vapours should be included in global climate models.

Appendix A

For particles that consist of several components the HGF of such mixed particle (HGF_m) can be estimated from the growth factors of the individual components of the particle and their respective volume fractions, applying the ZSR relation (Stokes and Robinson, 1966):

$$HGF_m = \left(\sum_k \epsilon_k HGF_k^3 \right)^{1/3} \quad (A1)$$

where the summation is performed over all of the compounds that are present in the particle. ϵ_k is the volume fraction and HGF_k is the hygroscopic growth factor of each of the components present in the particle.

The above simplified approach compared to full thermodynamic models is valid if there are no solute-solute interactions, i.e. that the water uptake of the mixed particle is equal to the sum of the individual water uptakes of each component. Correct treatment of the Kelvin effect within the ZSR relationship means to take the HGF_k at equal water activity as HGF_m , or in good approximation at equal RH and dry size as the mixed particle, with the former option used in this study. We have previously shown (Meyer et al., 2009) that for a mixture of photooxidation products of α -pinene and ammonium sulphate at RH's of 90% (above the deliquescence point of ammonium sulphate) there are no solute-solute interactions and that the ZSR approximation can be applied.

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Applying the ZSR relationship the HGF_m of such a mixed particle becomes:

$$HGF_m = \left((1 - \epsilon_{AS}) HGF_{SOA}^3 + \epsilon_{AS} HGF_{AS}^3 \right)^{1/3} \quad (A2)$$

where ϵ_{AS} is the volume fraction of ammonium sulphate; HGF_{SOA} and HGF_{AS} are the hygroscopic growth factors of pure SOA and ammonium sulphate respectively. HGF_{AS} is taken from ADDEM (Topping et al., 2005), whereas HGF_{SOA} is taken from the chamber measurements (see Fig. A1). It should be noted that HGF_{SOA} decreases slightly with increasing thermodenuder temperature. This temperature dependence was approximated with a polynomial expression and used during the fitting procedure. Further the measurements of pure SOA were not available at the equal dry size. For this reason the semi-empirical k-Kohler theory (Petters and Kreidenweis, 2007) was used to extrapolate the original measurement to the dry size required as input for the ZSR model.

For each thermodenuder temperature we have calculated HGF_m from Eq. (A2). Using the measured value of VFR (as shown on Fig. 3) we have calculated ϵ_{AS} . ϵ_{AS} increases with the increasing thermodenuder temperature as more SOA evaporates. Therefore ϵ_{AS} at thermodenuder temperature T_d is calculated as:

$$\epsilon_{AS} = \frac{V_{AS}}{V} = \frac{V_{AS}}{V_0} \frac{V_0}{V} = \frac{\epsilon_0}{VFR} \quad (A3)$$

where: V_{AS} is the volume of ammonium sulphate within the particle of volume V at thermodenuder temperature T_d ; V_0 is the initial volume of the particle (before heating in the thermodenuder) and $\epsilon_0 = \frac{V_{AS}}{V_0}$ being the volume fraction of ammonium sulphate at room temperature (the initial volume fraction of ammonium sulphate).

Once the particle has evaporated to a diameter such that ϵ_{AS} becomes equal to 1 (the particle consists only of ammonium sulphate) ϵ_{AS} , used in Eq. (A2), was assumed to be constant and equal to 1. The only variable parameter for the fitting procedure was ϵ_0 .

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Table 1. Ion and particle growth rates.

Day	Growth rate (ions) between 7–20 nm [nmh ⁻¹]	Formation rate J2 (ions) [cm ⁻³ s ⁻¹]
8.11.2006	9.06	0.26
9.11.2006	8.49	0.055
10.11.2006	6.48	0.23
11.11.2006	3.51	0.054

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Table 2. Fitted values of the initial volume fraction of ammonium sulphate (ϵ_0) for the 4 nucleation events analysed and the maximum calculated value of H_2SO_4 concentration during the nucleation events.

Day	ϵ_0 [%]	H_2SO_4 max [10^6 cm^{-3}]
8.11.2006	3.5	9.25
9.11.2006	5.9	7.32
10.11.2006	49.2	15.27
11.11.2006	3.5	6.5

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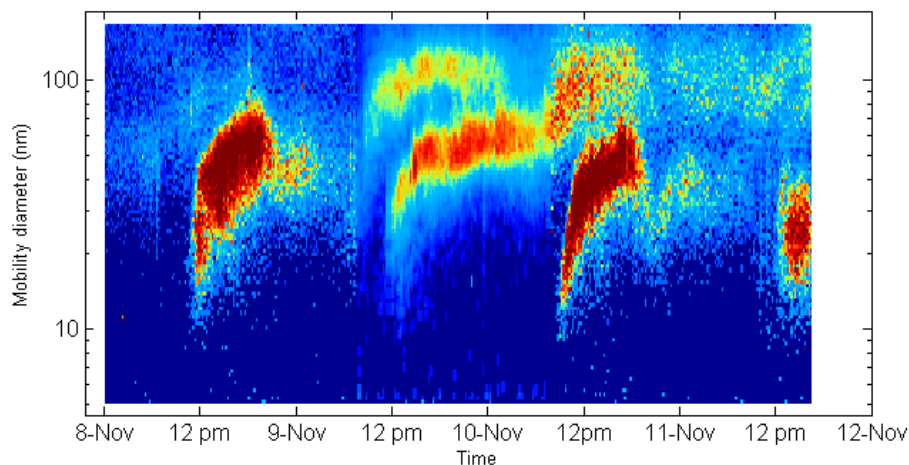


Fig. 1. Particle size distributions during the nucleation events measured by the SMPS in the size range from 5 to 168 nm.

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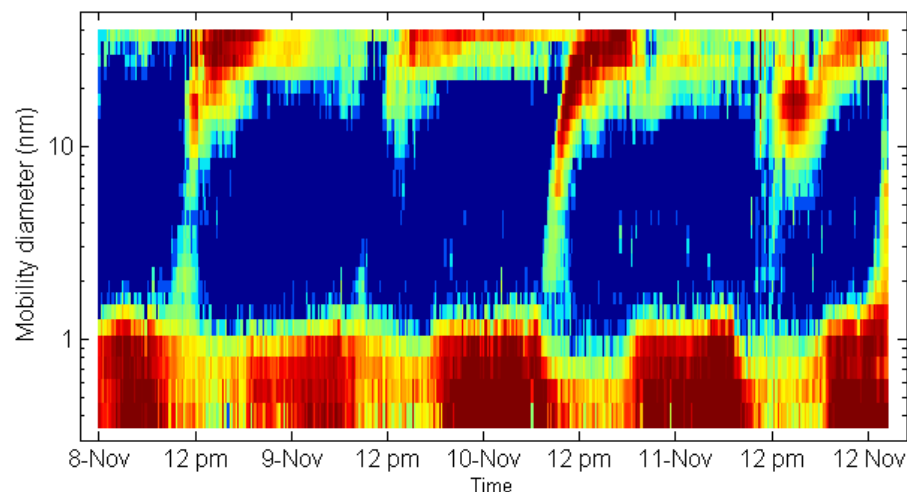


Fig. 2. Air ion size distributions during the nucleation events measured with the AIS in the size range from 0.34 to 40 nm.

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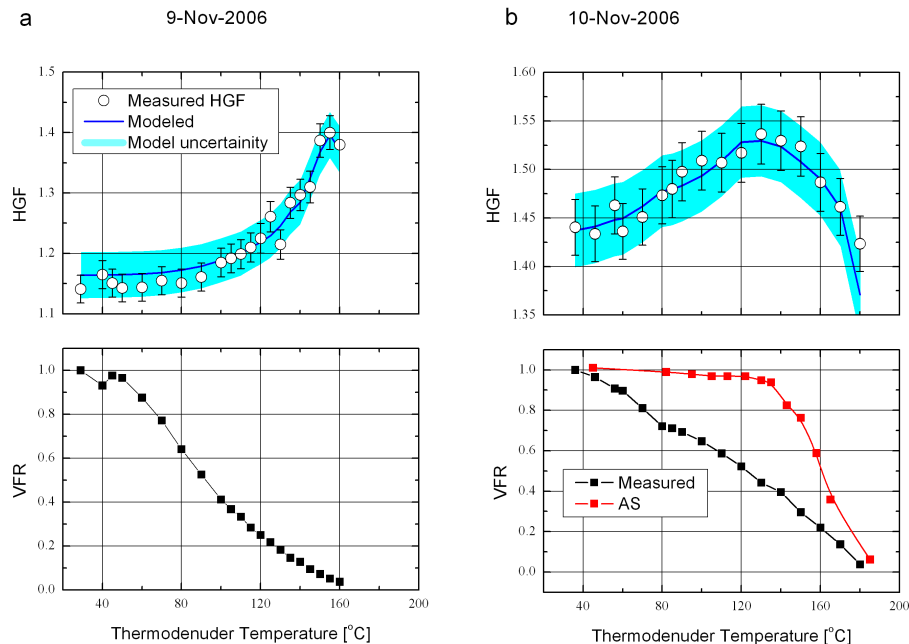


Fig. 3. VH-TDMA spectra. Dependence of the hygroscopic growth factors HGF (top graphs) and the volume fraction remaining $VFR=(D_v/D_{v0})^3$ (bottom graphs) as a function of the thermodenuder temperature for two nucleation events on 9 and 10 November. Initial particle size was 25 nm and the RH was kept constant at $90\%\pm0.2\%$. The fitted theoretical model of the HGF's (blue line) and the uncertainty (lower and upper confidence limits) (blue shaded region) are also shown. The error bars for the measured HGF on all figures are $\pm 2\%$ and come from the accuracy of particle sizing. In addition the volatilization curve of 30 nm ammonium sulphate (AS) particles is also presented (red line). Note that the reduction of hygroscopic growth in (b) corresponds to the volatilization of AS.

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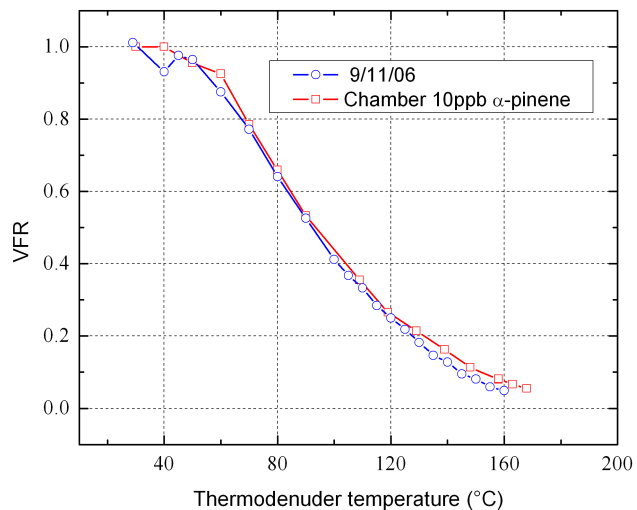


Fig. 4. Comparison with photochemical chamber experiments. Volatilisation of particles from a nucleation event observed on 9 November and from a photochemical chamber experiment with the photooxidation of α -pinene at a concentration of 10 ppb.

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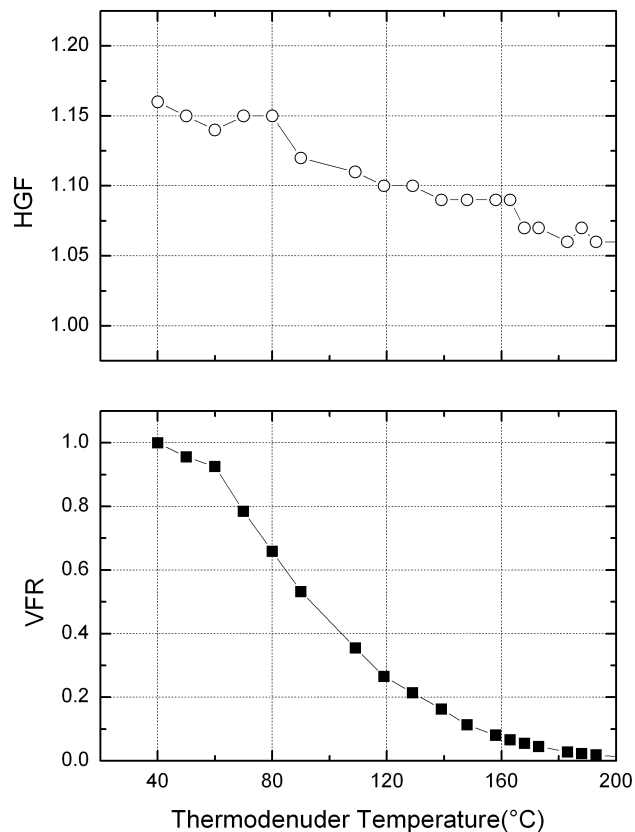


Fig. A1. Change in the hygroscopic growth factor (HGF) (upper graph) and volume fraction remaining (VFR) (lower graph) as a function of the thermodenuder temperature for particles generated in the smog chamber. Measurements were conducted at RH 90% and for initial particle size of 100 nm.

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