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**Hygroscopicity of
2–9 nm particles in
boreal forest**

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Applying the CPCB setup to study the hygroscopicity and composition of freshly-formed 2–9 nm particles in boreal forest

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Abstract

Measurements on the composition of nanometer-sized atmospheric particles are the key to understand which vapors participate in the secondary aerosol formation processes. Knowledge on these processes is crucial in assessing the climatic effects of secondary aerosol formation. We present data of >2 nm particle concentrations and their hygroscopicity measured with the Condensation Particle Counter Battery (CPCB) at a boreal forest site in Hyytiälä, Finland, during spring 2006. This is the first time such results on the hygroscopicity and composition of the freshly formed atmospheric clusters as small as 2 nm have been reported – bringing us closer to online measurements of the compounds participating in atmospheric particle formation. The data reveal that during new particle formation events, the smallest particles activate for growth at clearly smaller sizes in water than in butanol vapor. However, even at 2–4 nm, the particles are less hygroscopic than ammonium sulfate or sulfuric acid, which are often referred to as the most likely compounds present in atmospheric nucleation. This observation points to the presence of water-soluble organics, even at the very first steps on particle formation. The water-affinity of the particles decreases with size, indicating that the vapors that participate in the first steps of the particle formation and growth are more hygroscopic than the vapors contributing to the later stages of the growth. This suggests that the relative role of less hygroscopic organics in atmospheric particle growth increases as a function of particle size.

1 Introduction

Secondary aerosol formation via nucleation of atmospheric vapors is a global phenomenon proven to take place in a wide variety of environments (Kulmala et al., 2004a). The formed particles are likely to alter the Earth's radiation budget and therefore the climate significantly: after growing to large enough sizes (tens to hundreds of nanometers) the particles directly scatter solar radiation, and act as condensation nuclei for

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cloud droplets thus influencing the albedo and lifetime of the clouds (Ramanathan et al., 2001; Lohmann and Feichter, 2005). The Intergovernmental Panel on Climate Change stated in their latest report (IPCC, 2007) that the largest uncertainties limiting the scientific understanding of future and past climate changes relate to the climatic effects of aerosol particles. Besides their effect on the global climate, aerosols have a deteriorating impact on air quality, as they reduce visibility and cause adverse health effects. Boreal forests cover about 14% of the Earth's land area and have been observed to be a significant source of atmospheric aerosol particles (Dal Maso et al., 2005). In this study we will present data collected at a boreal forest site in Hyytiälä, southern Finland.

To accurately assess the magnitude of the particle source caused by secondary aerosol formation and growth in climate and air quality models, the main processes governing this phenomenon need to be known. It is still unclear in many respects what the nucleating or condensing atmospheric vapors are (Kulmala, 2003).

A major limitation in understanding the first steps of atmospheric particle formation has been the lack of atmospheric observations of electrically neutral aerosol particles with sizes close to 1 to 2 nm, the size range at which the nucleation and initial steps of the particle growth occurs. Therefore, a significant effort has recently been put into developing instruments that measure neutral atmospheric particles of 1–3 nm. Kulmala et al. (2007a) presented data on the concentrations of 2–3 nm and even smaller particles, based on measurements conducted with novel instruments (Neutral cluster and Air Ion Spectrometer, NAIS; and UF-02proto condensation particle counter). Sipilä et al. (2008) have made observations of atmospheric neutral clusters below 2 nm using the Pulse Height Condensation Particle Counter (PH-CPC) and Expansion-type Condensation Particle Counter (E-CPC). As emphasized also by Kulmala et al. (2007a), direct observations on atmospheric nucleation are crucial to pin down the particle formation processes in different environments. Proposed atmospheric nucleation mechanisms include kinetic, binary, ternary, ion-induced or ion-mediated nucleation, and the activation and growth of persistent neutral or charged molecular clusters (Hoppel et al.,

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1994; Yu and Turco, 2001; Lee et al., 2003; Kulmala et al., 2004a, 2006, 2007a).

Several laboratory and field studies suggest that sulfuric acid and sulfate clusters are likely participants in atmospheric nucleation and growth (Weber et al., 1997; Hanson and Eisele, 2002; Berndt et al., 2005; Sihto et al., 2006; Riipinen et al., 2007). However, there are also observations that imply that the ambient sulfuric acid concentrations cannot explain the observed nucleation and growth completely (Fiedler et al., 2005; Boy et al., 2005), particularly in rural environments. On the other hand, a clear link between atmospheric aerosol formation and the emissions of biogenic organics has been reported in several studies (O'Dowd et al., 2002; Kulmala et al., 2004b, 2004c; Tunved et al., 2006).

The key to the quantification of the compounds participating in the atmospheric particle formation would naturally be direct and accurate measurements of the composition of the freshly formed aerosol particles and clusters. These kinds of measurements, however, are challenging because of the minuscule masses of the freshly formed particles and limited duration of the particle formation events (of the order of hours). Therefore direct measurements on the particle composition, e.g. filter sampling and mass spectrometric studies, are typically limited to size ranges above 30–40 nm.

Recent mass spectrometric studies on the composition of nucleation mode particles include e.g. those by Zhang et al. (2004), Smith et al. (2005), and Allan et al. (2006). The two preceding papers studied nucleation mode particles in Pittsburgh and Atlanta, US, and reported sulfuric acid or ammonium sulfate as the predominant species in the aerosol, Smith et al. (2005) measuring particles even as small as 10 nm. The latter study analysed particle formation and growth events in Hyytiälä, concluding that during the condensational growth process, the sub-100 nm particles were principally organic in composition, although also sulfates were present in significant amounts. Mäkelä et al. (2001) observed increased amounts of dimethylamine in the accumulation mode particles during particle formation events compared to non-events, based on samples collected by a cascade impactor and analysed using ion chromatography.

Because of the difficulties in direct particle composition measurements below 20 nm,

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indirect methods such as measurement of particle volatility or hygroscopicity are often used. However, also the conventional hygroscopicity and volatility measurement setups (e.g. Hygroscopicity Tandem Differential Mobility Analyzer, HTDMA; Volatility Tandem Differential Mobility Analyzer, VTDMA) are limited to larger than approximately 10 nm particles in atmospheric conditions, due to the relatively low concentrations of the small particles, particularly in remote conditions. Sakurai et al. (2005) reported hygroscopicity results even down to 4 nm for an urban site in Atlanta, and concluded that the freshly-formed particles in this rather polluted site were most likely consisting mainly of ammonium sulfate. Ehn et al. (2007a) measured the hygroscopicity of aerosol particles down to 10 nm in Hyytiälä, and observed a clear correlation between the hygroscopicity of the growing aerosol mode and ambient sulfuric acid concentrations. They also observed that as the freshly formed aerosol was growing further, its hygroscopicity decreased, indicating the condensation of a less hygroscopic, probably organic (e.g. Varutbangkul et al., 2006), species. O'Dowd et al. (2002) presented a comparison of ambient Pulse Height-CPC (Saros et al., 1996) spectra to those produced by ammonium sulfate, pinic and cis-pinonic acids, concluding that ammonium sulfate is not likely to be the main constituent of 3–5 nm particles in Hyytiälä, but that the particles are rather consisting mainly of organics. Kulmala et al. (2004b), on the other hand, suggested that sulfurous compounds contribute to the initial steps of particle formation and growth, whereas organics participate in the later stages of the growth. To resolve the questions raised by the afore-mentioned studies on the relative role of sulfuric acid and organics in different stages of particle formation and growth, more measurements on the composition of sub-10 nm particles are needed.

Recently Kulmala et al. (2007b) presented a novel instrumental setup, the Condensation Particle Counter Battery (CPCB), which can be used to study the concentrations and constituents of particles even smaller than 3 nm. The CPCB consists of four Condensation Particle Counters (CPCs, see e.g. McMurry, 2000), two working with butanol (TSI-3010 and TSI-3025, also referred to as CPC and UCPC) and two with water (TSI-3875 and TSI-3786, or WCPC and UWPC) as the condensing vapor. The different

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vapors lead to differences in the sizes of the smallest detected particles, depending on the composition of the sampled aerosol. If the smallest particles have a higher affinity for water than for butanol, the 50% cut-off sizes (D_{50}) of the water-CPCs are lowered compared to the butanol-CPCs. This is observed as increased particle concentrations detected by the water-CPC in comparison with the butanol-CPC with the same cut-off size for insoluble (e.g. silver) particles. Highly water soluble particles (sodium chloride, ammonium sulfate) have been observed to decrease the detection limits of the water-CPCs significantly (Hering et al., 2005; Petäjä et al., 2006; Kulmala et al., 2007b). Such clear dependence on the water-solubility of the sample has not been observed for the cut-off sizes of the butanol-CPCs (see e.g. Sem, 2002).

We present data collected with the CPCB in March–May 2006 in Hyytiälä, Finland (Hari and Kulmala, 2005). The affinity of freshly-formed 2–9 nm particles to water or butanol is investigated by comparing the concentrations measured by the two CPC pairs of the CPCB. We estimate the ambient 50% cut-off sizes of the CPC pairs and using this data assess the water solubility of the 2–9 nm particles. Finally, the relative roles of sulfurous compounds and organics in particle formation and growth are discussed. In this study we continue the effort of direct measurements of atmospheric nucleation processes, and complement the work by Kulmala et al. (2007a) by investigating the composition of the sub-3 nm atmospheric particles.

2 Materials and methods

The field measurements were conducted at the SMEAR II station in Hyytiälä, Southern Finland (61°51′N, 24°17′E, 181 m a.s.l., Hari and Kulmala, 2005) during 6 March–31 May 2006. The station is located in a boreal forest with Scots Pine as the dominating species, and is equipped with various continuous measurements on atmospheric composition and dynamics and atmosphere-biosphere interactions. Atmospheric new particle formation and growth events are observed at the SMEAR II station on 60–120 days a year (Dal Maso et al., 2005), and the frequency of these events has its

maximum during the spring. Data from measurements with the Condensation Particle Counter Battery (CPCB), Neutral cluster and Air Ion Spectrometer (NAIS) and Differential Mobility Particle Sizer (DMPS) systems form the basis of the analysis presented in this work.

5 2.1 Instrument description

2.1.1 Condensation Particle Counter Battery (CPCB)

Condensation Particle Counter (CPC) is an instrument which measures the number concentration of aerosol particles online, typically with a time resolution of the order of seconds. The working principle of the CPC is based on three processes: 1) creation of a supersaturated vapor (working fluid), 2) growth of aerosol particles by condensation of these supersaturated vapors, 3) optical detection of the particles after their growth. Different types of CPCs have different techniques of creating vapor supersaturation. The most common type is the laminar flow chamber CPC, which has no movable parts and therefore is suitable for long-term atmospheric observations. Recent developments of CPCs in general have aimed, for instance, at improving the detection efficiency (Stoltzenburgh and McMurry, 1991) and response time (Sgro and Fernández de la Mora, 2004). For a comprehensive summary of the history and principles of CPCs see e.g. McMurry (2000).

The Condensation Particle Counter Battery (CPCB, Kulmala et al., 2007b) is composed of four individual CPCs, which are operated in parallel. Figure 1 shows the arrangement of the four CPCs, which represent a 2×2 matrix of different cut-off sizes, as well as different working liquids (n-butanol and water). As indicated in Fig. 1, the pair of CPCs (TSI-3010, TSI-3785) as well as the pair of UCPCs (TSI-3025, TSI-3786) is designed so that the same count rates are expected for particle materials that show affinity neither to water nor to butanol. Owing to the increased activation probability in water vapor, however, hygroscopic particles will be detected down to lower particle sizes in the water-CPCs; therefore an increased count rate will be measured in compar-

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ison to the butanol-CPCs. The differential signal between the water and butanol-CPCs of each pair is then expected to be related to the presence of hygroscopic particles in the size range of the corresponding cut-off regions. For lipophilic particles, the reverse may be true: if the activation probability of lipophilic particles is higher in butanol vapor than in water, the CPCB will be sensitive to the presence of lipophilic particles in the size range of the two cut-offs.

To determine the “reference state” of the CPCB for insoluble particles, the detection efficiencies of all four CPCs were carefully measured in the calibration set-up presented by Mordas et al. (2005). Briefly, practically monodisperse and spherical silver particles below 40 nm were generated by a combination of a furnace generator and a differential mobility analyzer (Scheibel and Porstendörfer, 1983). Before measuring in the field, the cut-off sizes of the two butanol-CPCs, the TSI-3025 and the TSI-3010, were determined to be 3.8 ± 0.3 and 8.7 ± 0.3 nm, respectively. The cut-off sizes of the two water-CPCs, the TSI-3786 and the TSI-3785, were adjusted so that they matched exactly the cut-off of the corresponding butanol-CPCs. In practice this was achieved by varying the temperature difference between the saturator and the growth tube inside the water-CPCs (Petäjä et al., 2006) until agreement between the cut-off diameters was reached. The particular temperature differences were 71 K for the TSI 3786, and 34 K for the TSI 3785, and were used as operational values during all subsequent experiments. The detection efficiencies of the CPCs in the CPCB before the field measurement campaign are presented in Fig. 2.

The ambient aerosol particle concentrations were monitored at the SMEAR II station during 6 March–31 May 2006 with all the four CPCs of the CPCB continuously and simultaneously, the time resolution of the instruments being 10 s. However, shortly after the beginning of the measurements (14 March 2006) the TSI-3010 CPC needed to be replaced with a new instrument having a D_{50} of 10.7 ± 0.3 nm, being slightly higher than the D_{50} of the corresponding WCPC.

After the field measurements the CPCB was calibrated again to see whether significant changes in the detection efficiencies had occurred during the measurement

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period. The cut-off sizes after the measurement period were 3.8 ± 0.3 nm (UCPC), 2.9 ± 0.3 nm (UWCPC), 10.5 ± 0.3 nm (CPC) and 9.1 ± 0.3 nm (WCPC), indicating that all the instruments stayed rather stable throughout the measurement period. The detection efficiency curves of the CPCs after the measurement campaign are presented in Fig. 3.

2.1.2 Neutral cluster and Air Ion Spectrometer (NAIS)

The NAIS is an instrument which measures mobility distributions of neutral and charged aerosol particles and clusters in the range from 2.39 to $0.0010 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This corresponds to a diameter range of approximately 0.8 to 47 nm in mobility equivalent diameter (Kulmala et al., 2007a). The working principle of the NAIS is based on unipolar charging of sampled particles and their subsequent classification with an electrical mobility analyzer and detection with a set of electrometers. The time resolution of the NAIS is 5 min.

The NAIS is developed from the Air Ion Spectrometer (AIS, Airel Ltd., Estonia, Mirme et al., 2007). It has 21 electrometer rings in the inside-out differential mobility analyzers. Unlike the AIS, the NAIS has two unipolar corona chargers prior to the mobility analyzers – one for positive and one for negative charging – and electrostatic post-filters. These post-filters are used to remove excess ions generated by the chargers. The particle charging probabilities are estimated from Fuchs' theory (Fuchs and Sutugin, 1970). The lower detection limit of the NAIS is determined by the charging probabilities, cluster concentration, and the charger ion masses and mobilities. The charger ion mobilities from 1.3 to $1.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ define the lowest estimation for the detection limit, which is approximately 2 nm. Particles below this limit cannot reliably be distinguished from the charger ions.

The sample and sheath flows of the analyzers are 0.5 l s^{-1} and 1 l s^{-1} , respectively. A closed loop sheath flow arrangement is used in both analyzers. The noise and the offset of the electrometers are measured by sampling through a second filter consisting of a unipolar corona charger and an electrostatic filter. Similar filtration is used also for

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cleaning the re-circulated sheath air.

2.1.3 Differential Mobility Particle Sizer (DMPS) system

Continuous particle size distribution measurements between 3 and 1000 nm have been carried out with a Differential Mobility Particle Sizer (DMPS) system since 1996 at the SMEAR II station. The setup in Hyytiälä is a twin-DMPS, consisting of two separate DMPS systems: the first DMPS measures particles starting from 3 nm (applying a TSI-3025 CPC), and the second from 10 nm (with a TSI-3010 CPC). The sheath flows in the system are maintained using a closed-loop arrangement (Jokinen and Mäkelä, 1997). For a detailed description of the DMPS setup applied in Hyytiälä, we direct the reader to Aalto et al. (2001).

2.2 Data processing

In the data analysis we averaged the data over 5 min periods. Because of minor drifts in the flows inside the CPCs during the measurement period, the WCPC/CPC and UWPC/UCPC concentration ratios were normalised to unity during the nights when no particles in the size range 3–10 nm were observed.

To obtain estimates for the ambient cut-off sizes of the WCPC, we compared the obtained CPCB data with the DMPS data. The comparison was done by weighting the DMPS size distribution data with the detection efficiency curves of the CPCs (see Figs. 2 and 3) and thus calculating the WCPC/CPC concentration ratio prediction corresponding to particles with equal affinity to butanol and water. This prediction was then compared with the measured WCPC/CPC concentration ratio. The cut-off size of the WCPC was then estimated by shifting the detection efficiency curve towards smaller sizes to make the measured and predicted concentrations match. To get the maximum estimate for the D_{50} in the WCPC we assumed that the ambient cut-off size of the butanol-CPC is close to that determined for insoluble particles.

The obtained ambient D_{50} values were compared to the D_{50} values for insoluble

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particles to yield the corresponding hygroscopic growth factors

$$GF = \frac{D_{50,wet}}{D_{50,dry}} \quad (1)$$

of the freshly nucleated inside the saturator of the water-CPCs, where RH is close to 100%. $D_{50,dry}$ is the cut-off size for corresponding insoluble particles, whereas $D_{50,wet}$ refers to the cut-off size for the hygroscopic particles, as they are assumed to grow in the saturator. It should be borne in mind, however, that this approach for estimating the GF only accounts for the effect of the particle size on the activation probability inside the condenser of the water-CPCs, assuming that the effect of the particle composition is mainly due to the different hygroscopic growth inside the saturator. Therefore the obtained estimations for the growth factors should be treated as indicative rather than as absolute numbers. The effect of the curvature on the growth of the droplet was taken into account by normalizing the GF values obtained directly from the measurements with the Kelvin effect for water (see e.g. Swietlicki et al., 2008)

$$GF_{\text{eff}} = 1 + (GF - 1) \cdot \exp\left(\frac{4M\sigma}{RTD\rho}\right), \quad (2)$$

where σ is the surface tension of the droplet, ρ is its density, M the molar mass, R the molar gas constant, T the temperature and D the diameter of the droplet. Since we could not assume anything about the droplet composition, we assumed the surface tension and density of the droplet to be close to those of water.

Similar analysis as described above for the DMPS data was done comparing the UWPCP/UCPC concentration ratios and the size distributions measured with the NAIS (Kulmala et al., 2007a). This comparison provides a reference of the total particle concentrations down to 2 nm and therefore allows for estimates on the ambient cut-off sizes of the UWPCP/UCPC pair as well as growth factors inside the UWPCP.

The ambient cut-off sizes of the CPCB were estimated also using lognormal size distribution fits done for the DMPS data. If a clear growing nucleation mode was present,

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the fitted nucleation mode was extrapolated to sizes below 2 nm to obtain a reference for the sub-3 nm size range. The simulated mode was weighted with the detection efficiency functions and compared to the particle concentrations observed with the water/butanol-CPC pairs. It was assumed that the shape and growth rate of the nucleation mode stayed relatively constant also during the first steps of the nucleation to be able to assess the lowest detection limit of the CPCB. In all the cut-off size analyses described above, we used the averages of the detection efficiency curves measured before and after the measurement campaign.

To further study implications on the hygroscopicity and composition of the freshly formed nucleation mode, the CPCB data was compared with the results obtained from the HTDMA measurements conducted in Hyytiälä during spring 2005 (Ehn et al., 2007a). Comparison was also done with the ambient sulfuric acid concentrations and the fraction of particle growth rates at 1.3–3 nm and 3–7 nm explained by the condensation of sulfuric acid. Estimations for the ambient sulfuric acid concentrations were calculated with a quasi-steady state model (Boy et al., 2005). The growth rates for 1.3–3 and 3–7 nm particles were determined from the ionspectrometer data continuously measured in Hyytiälä (Hirsikko et al., 2005). The theoretical growth rates at 1.3–3 and 3–7 nm caused by the ambient sulfuric acid concentrations were calculated as presented by Lehtinen and Kulmala (2003).

3 Results and discussion

Typical data measured by the CPCB on new particle formation (NPF) event and non-event days are illustrated in Fig. 4. The figure shows the total concentrations measured by the CPCB and ratios of concentrations measured by the water- and butanol-CPCs on two example periods – 20–23 March 2006 (left panel); 21–24 May 2006 (right panel)– along with the corresponding particle size distributions between 3 and 1000 nm as measured by the DMPS. The first period consists of four consecutive days with clear NPF events, whereas the second contains four consecutive days with no clear indica-

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tions of new particle formation and growth in the smallest size range. On all the days with indications of new particle formation and growth, the water-CPCs measured more particles than the butanol-CPCs, suggesting that their cut-off size was lowered relative to the butanol-CPCs, see Fig. 4 (left panel), and thus that the freshly nucleated particles have a higher affinity for water than butanol. On the days that had not been classified as NPF event days, no systematic differences were observed, see Fig. 4 (right panel). The same behavior can be seen in Fig. 5, which shows the median diurnal behavior of the UWPC/UCPC and WCPC/CPC concentration ratios on the 32 NPF event and 15 non-event days over the whole measurement period. The WCPC/CPC concentration ratio is typically slightly higher than the UWPC/UCPC ratio. At least part of this can be explained by the fact that during most of the measurement period the CPC measured with a slightly higher cut-off size (also for insoluble particles) than the WCPC, whereas the cut-off sizes of the UWPC and UCPC matched better (see Figs. 2 and 3).

The ambient cut-off sizes of the WCPC and UWPC during particle formation episodes were determined by comparing the CPCB data to the size distributions measured by the DMPS and NAIS, as well as to size distributions obtained by lognormal fits to DMPS data. Figure 6 illustrates this analysis for a particle formation event on 23 April 2006. The top panel indicates the size distribution data measured by the DMPS. The total concentration measured by the DMPS system, the concentrations obtained from the DMPS size distribution weighted with the WCPC and CPC detection efficiency curves (see Figs. 2 and 3), and the concentrations measured by the WCPC and CPC are shown in the middle panel. The bottom panel shows the measured WCPC/CPC concentration ratio along with the ratios predicted from the DMPS data assuming either no shift in the WCPC cut-off size or that $D_{50}=7.5$ nm (1.5 nm shift compared to insoluble silver particles), corresponding to the best match with the measured concentration ratio. The shift in the cut-off size can be used to estimate the effective hygroscopic growth factor inside the WCPC, GF_{eff} . In the best-match case presented in Fig. 6, $GF_{\text{eff}}=1.4$. A similar example for the ultrafine CPCs and NAIS comparison is shown in Fig. 7 for a particle formation event on 20.3.2006, now yielding $D_{50}=2.7$ (0.9 nm shift compared

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to insoluble particles) and $GF_{\text{eff}}=1.4$ for the UWPC. Although D_{50} and GF_{eff} are likely to vary during the day, usually only one value per day was fitted for both parameters. Only if two very distinct peaks in the concentration ratios were observed, two values are reported. On these kinds of days, it was noted that the later value of D_{50} was always larger than the earlier, corresponding to lower hygroscopic growth factor as the aerosol grows in size and ages during the day.

As can be seen from Figs. 6 and 7, the temporal evolution of the measured concentration ratios can typically be predicted quite well from the DMPS and NAIS size distribution data. The detailed analysis also verifies that usually the differences in the concentrations measured by the water and butanol-CPCs cannot be explained only by the different shapes of the detection efficiency functions (Figs. 2 and 3), but in fact a shift in the D_{50} of the water-CPCs is needed to reproduce the measured data. Also the butanol-CPCs tend to measure slightly higher concentrations than predicted by simply weighting the DMPS or NAIS size distributions with the detection efficiencies for totally insoluble silver particles (middle panel in Figs. 6 and 7). One reason for this could be that the ambient cut-off size of the butanol-CPC is also somewhat shifted compared to that of totally insoluble particles.

Figure 8 shows the ambient D_{50} values determined for the whole measurement period with different methods. The left panel contains the cut-off sizes determined for the WCPC from the DMPS data and the corresponding size distribution fits. The right panel contains the cut-off sizes of the UWPC obtained from the NAIS data with positive and negative charging of the sample (Kulmala et al., 2007a), as well as from the size distribution fits to DMPS data. The methods yield consistent results, giving 7.1–7.2 nm and 2.5–2.6 nm as the median values of the ambient cut-off sizes of the WCPC and UWPC, respectively. The corresponding shifts in the cut-off sizes compared to insoluble particles are thus 1.8–1.9 and 0.8–0.9 nm. As these values correspond to the averages of detection efficiency curves before and after the measurements, uncertainties of approximately 0.3 nm should be taken into account. Also, the values should be considered as maximum estimates, as no shift for the ambient D_{50} values of the

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butanol-CPCs was assumed. It can also be noted from Fig. 8 that the cut-off size of the WCPC varies much more from day to day than the corresponding values for the UWPC. It is possible that the composition of the smallest particles varies less from day to day, whereas in the larger sizes there are more different vapors contributing to their growth on different days. Also the Kelvin effect of the smaller particles is larger, making the detection efficiency less sensitive to the composition of the particles in comparison with their size.

Figure 9 contains the effective hygroscopic growth factors inside the water-CPCs obtained from the D_{50} values, and normalized with respect to the particle size. Again, all the different approaches give similar results, yielding a median GF_{eff} of 1.4 for the WCPC and 1.6–1.7 for the UWPC. One must be careful, however, when interpreting the data, as these growth factors would correspond to the case where the particle size is the main factor limiting the activation in the growth tube of the water-CPCs. This is likely not to be exactly the case, as also the composition of the droplets probably plays a role also in the growth tube. The growth factors presented here should thus be treated as indicative rather than exact numbers. However, the results for the WCPC are somewhat similar with results obtained from HTDMA data from Hyytiälä: Ehn et al. (2007a) report hygroscopic growth factors of roughly 1.2–1.4 for 10 nm particles at 88% relative humidity, which would correspond to 1.3–1.5, if normalized with respect to particle size (see Eq. 2).

The slightly higher growth factors for the smaller sizes indicate higher hygroscopicity as compared with the larger, more aged particles, implying that the vapors participating in the later stages of the particles growth are less hygroscopic than the vapors responsible for the initial steps of particle formation and growth. This supports the idea presented by e.g. Kulmala et al. (2004b) and Hirsikko et al. (2005), suggesting that the relative role of organic compounds compared to e.g. sulfurous substances increases with increasing size. It is also possible that the condensing organics oligomerize (Kalberer et al., 2004), which is catalysed by particulate phase sulfuric acid (Jang et al., 2002), and form a non-volatile – and probably also less hygroscopic – growing

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core to the particle, as has been observed also in previous studies (Kalberer et al., 2002; Wehner et al., 2005; Ehn et al., 2007b).

As ammonium sulfate has been observed to be a major component of atmospheric nanoparticles (Hanson and Eisele, 2002; Smith et al., 2005; Sakurai et al., 2005), the obtained GF_{eff} values were compared with UWPC detection efficiency curves obtained for pure laboratory-generated ammonium sulfate particles (Kulmala et al., 2007b). Kulmala et al. (2007b) observed that the D_{50} of the UWPC decreased from 3 nm to 2.3 nm, if ammonium sulfate aerosol was used instead of silver particles. This would correspond to a GF_{eff} larger than 1.8, indicating that even though clearly water soluble, the ambient aerosol near 3 nm is usually less hygroscopic than ammonium sulfate. This observation points to the possible role of water-soluble organics even in the very initial steps of aerosol growth, although, as noted above, their influence gets larger as the particles grow further. There were days however, when effective growth factors of 1.8 and even larger were observed (see Fig. 9). On these days the hygroscopic properties of the freshly formed aerosol do resemble those of ammonium sulfate.

We also investigated the possible relation between modeled sulfuric acid concentrations (Boy et al., 2005) and the hygroscopicity of the freshly formed particles. In Fig. 10 the ambient cut-off sizes of the water-CPCs are plotted against the sulfuric acid concentration and the fraction of the 1.3–3 (in the case of UWPC) and 3–7 nm (in the case of WCPC) growth rates explained by the condensation of sulfuric acid. The cut-off sizes of the WCPC show a very clear negative correlation with sulfuric acid. This is expected, as sulfates are very hygroscopic (Hämeri et al., 2001). In the case of the UWPC not such a clear correlation is seen. This observation suggests that at the smaller sizes sulfuric acid alone does not seem to control the hygroscopicity of the particles. At the larger sizes, on the other hand, the hygroscopicity seems to be controlled by sulfuric acid concentrations. The fraction of growth rates explained by sulfuric acid condensation is typically of the order of 10% and even less in the case of 3–7 nm particles, whereas at 1.3–3 nm the fraction ranges between 10 to 100%. However, even

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at the smallest sizes, the cases where sulfuric acid could explain the observed growth rates totally are very few. Thus some other condensing vapors, presumably organics, are needed to participate in the growth process also in sizes close to 1.3–3 nm.

4 Conclusions

5 We conducted measurements on the hygroscopicity of freshly-nucleated 2–9 nm particles with the Condensation Particle Counter Battery (CPCB) at a boreal forest site in Hyytiälä, Finland. Based on the data, two main conclusions could be made. First, it was observed that the freshly-formed aerosol was more hygroscopic at sizes close to 3 nm than at 9 nm, suggesting that the role of organics in the condensational growth of
10 particles increased with the particle size. Second, it was noted that the contribution of organics was needed to explain the results even at sizes close to 3 nm: the ambient aerosol seemed to be less hygroscopic than pure ammonium sulfate or sulfuric acid.

With these results on the composition of >2 nm particles we complement the work begun by Kulmala et al. (2007a) where the concentrations of the atmospheric pre-nucleation clusters and freshly nucleated particles were directly observed. Our results give indications on the relative role of sulfurous versus organic compounds in
15 atmospheric particle formation and growth, being related to e.g. anthropogenic versus biogenic influence on atmospheric aerosol budgets. However, to accurately quantify the composition of the nanometer-sized particles and the identities of the nucleating vapours, more CPC calibrations and studies on the activation behavior of particles
20 containing atmospherically relevant compounds, particularly organics, are needed.

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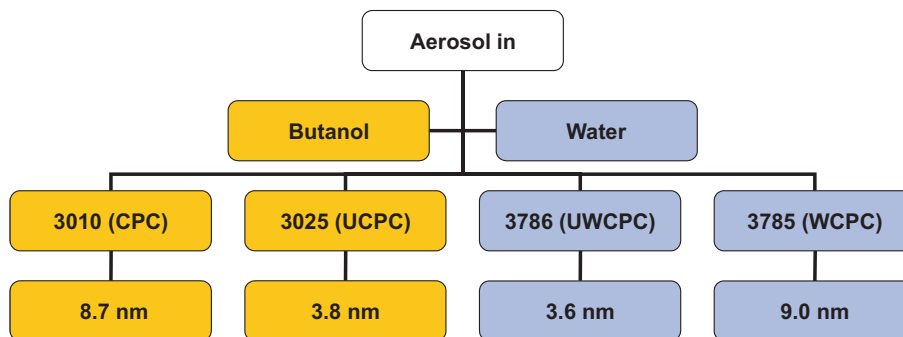


Fig. 1. A schematic figure of the setup of Condensation Particle Counter Battery (CPCB) used in this study. The CPCs using butanol as the working fluid are presented on yellow background, whereas the water-CPCs are on the blue background. The cut-off sizes set before the field measurements with silver particles are indicated under each individual CPC.

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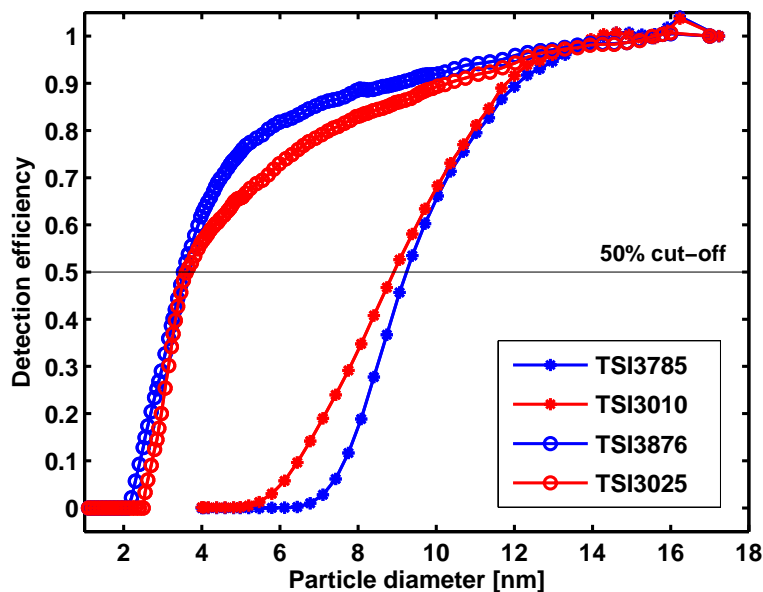


Fig. 2. The detection efficiencies of the individual CPCs in the CPCB, as measured for insoluble silver particles before the measurement campaign in Hyytiälä. Water-CPCs are indicated in blue and butanol-CPCs in red. The black line indicates the 50% detection efficiency limit (corresponding to the cut-off sizes D_{50}).

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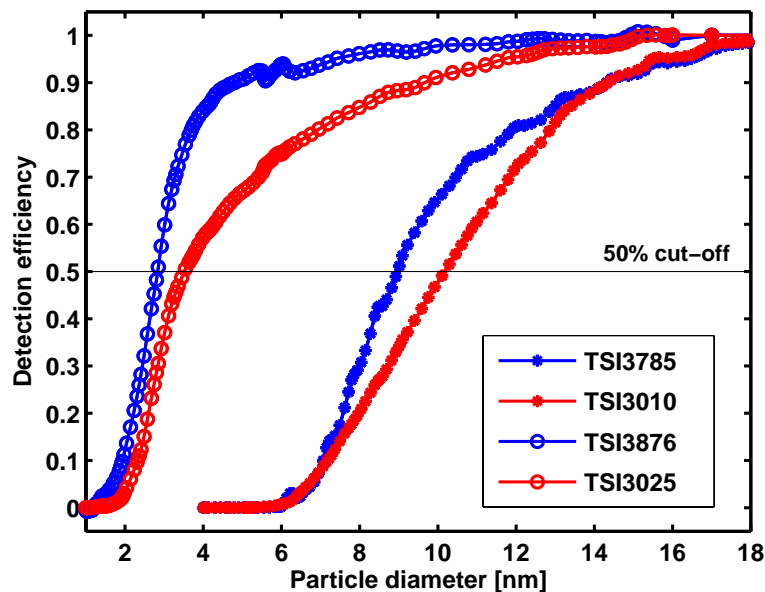


Fig. 3. The detection efficiencies of the individual CPCs in the CPCB, as measured for insoluble silver particles after the measurement campaign in Hyytiälä. Water-CPCs are indicated in blue and butanol-CPCs in red. The black line indicates the 50% detection efficiency limit (corresponding to the cut-off sizes D_{50}).

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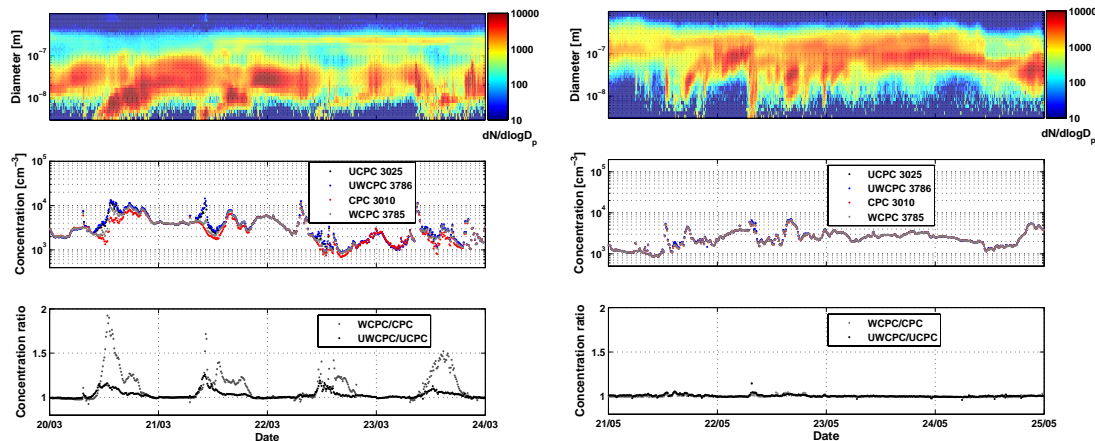


Fig. 4. Particle concentrations (middle) and water- to butanol-CPC concentration ratios (bottom) measured by the CPCB on **(a)** the period 20–23 March 2006 of four consecutive NPF event days; **(b)** the period 21–24 May 2006 of four consecutive days with no clear indications of NPF or growth. The corresponding particle size distributions measured with the DMPS are presented for comparison (top).

Particle concentrations (middle) and water- to butanol-CPC concentration ratios (bottom) measured by the CPCB on the period 20–23 March 2006 of four consecutive NPF event days (left panel); the period 21–24 May 2006 of four consecutive days with no clear indications of NPF or growth (right panel). The corresponding particle size distributions measured with the DMPS are presented for comparison (top).

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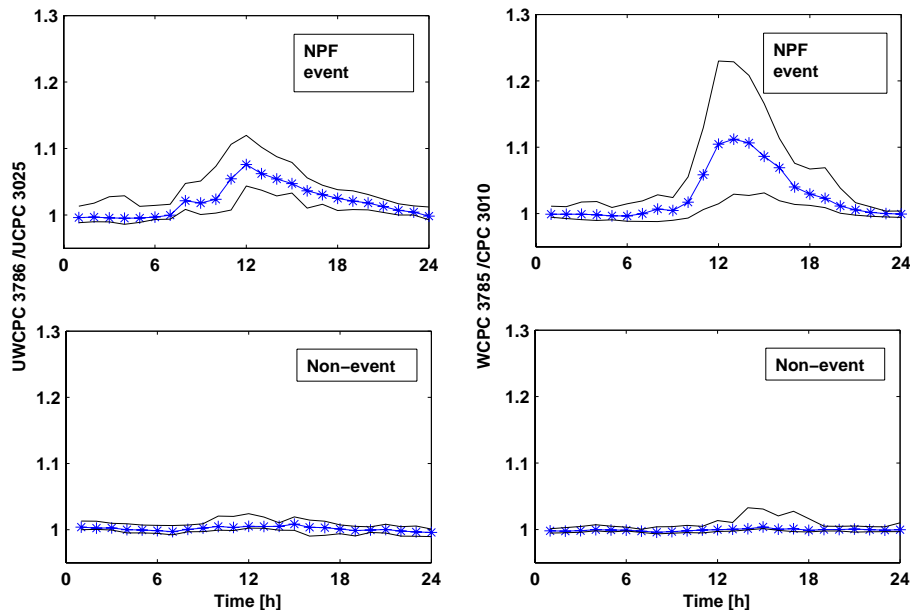


Fig. 5. The median (blue) diurnal behavior of the UWPC/UCPC (left) and WCPC/CPC (right) ratios on NPF event (top) and non-event (bottom) days during the measurement period in spring 2006. The black lines refer to the 25- and 75-percentiles.

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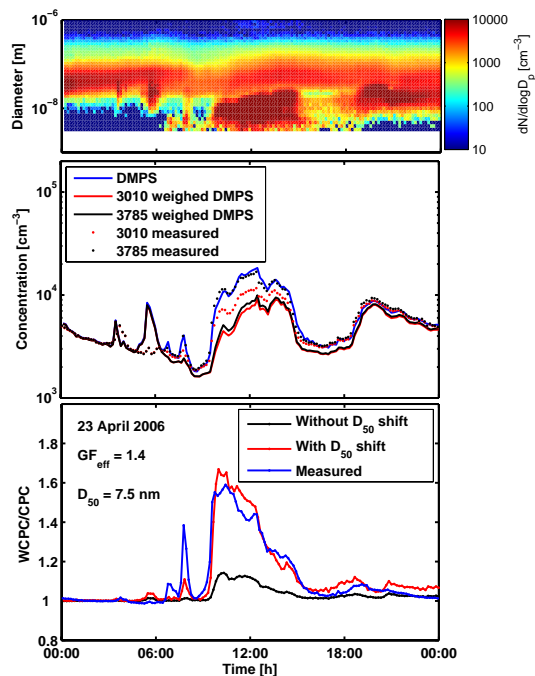


Fig. 6. Comparison between DMPS size distribution data and the concentrations measured by WCPC and CPC on a particle formation event day on 23 April 2006. Top: the size distributions measured by the DMPS. Middle: the total concentration measured by the DMPS (blue curve), the concentrations corresponding to the DMPS size distribution weighted with the detection efficiency curves of the WCPC (black curve) and CPC (red curve) for insoluble particles, and the total concentrations measured by the WCPC (black dots) and CPC (red dots). Bottom: the measured WCPC to CPC concentration ratio (blue) and as predicted from the DMPS data assuming 1) the detection efficiency curves according to calibrations with insoluble particles (black); 2) the cut-off size of the WCPC to be shifted to 7.5 nm (red).

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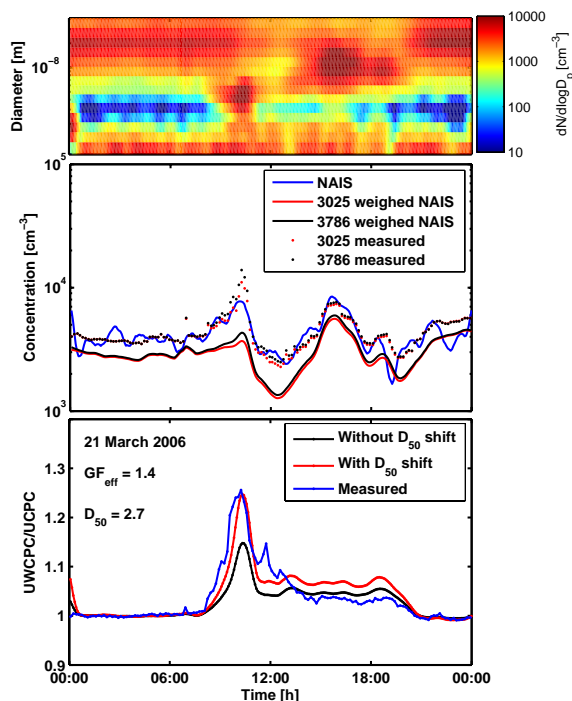


Fig. 7. Comparison between NAIS size distribution data and the concentrations measured by UWPCP and UCPC on a particle formation event day on 21 March 2006. Top: the size distributions measured by the NAIS. Middle: the total concentration measured by the NAIS (blue curve), the concentrations corresponding to the NAIS size distribution weighted with the detection efficiency curves of the UWPCP (black curve) and UCPC (red curve) for insoluble particles, and the total concentrations measured by the UWPCP (black dots) and UCPC (red dots). Bottom: the measured UWPCP to UCPC concentration ratio (blue) as predicted from the NAIS data assuming 1) the detection efficiency curves according to calibrations with insoluble particles (black); 2) the cut-off size of the UWPCP to be shifted to 2.7 nm (red).

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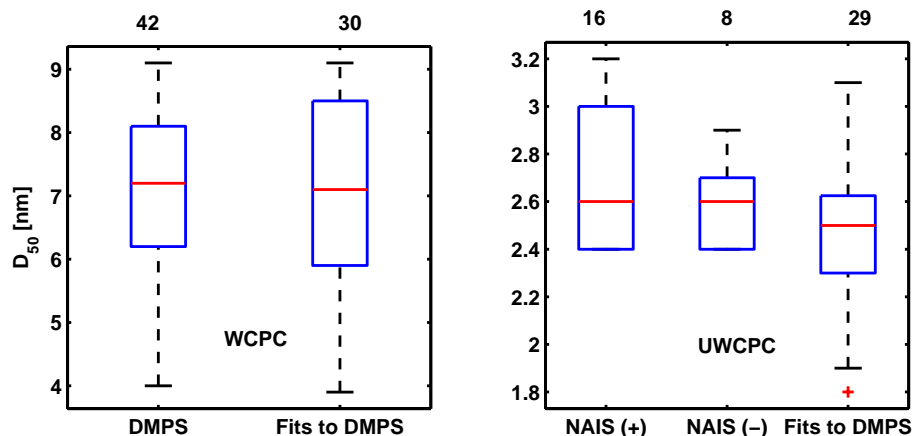


Fig. 8. The ambient 50% cut-off sizes of the WCPC (left) and UWPC (right) during NPF events in spring 2006, as obtained with different methods. The numbers above the figures refer to the number of particle formation event days included in the analysis. The red lines show the medians, the boxes indicate the 25- and 75-percentiles, and the error bars the 5- and 95-percentiles.

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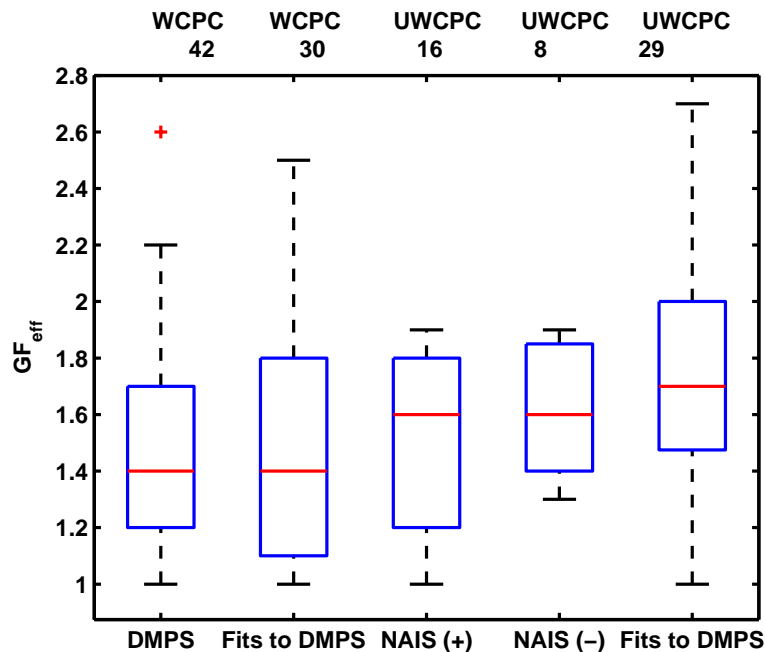


Fig. 9. The effective growth factors inside the WPCP and UWPCP during NPF events in spring 2006 according to different methods. The numbers above the figures refer to the number of particle formation event days included in the analysis. The red lines show the medians, the boxes indicate the 25- and 75-percentiles, and the error bars the 5- and 95-percentiles.

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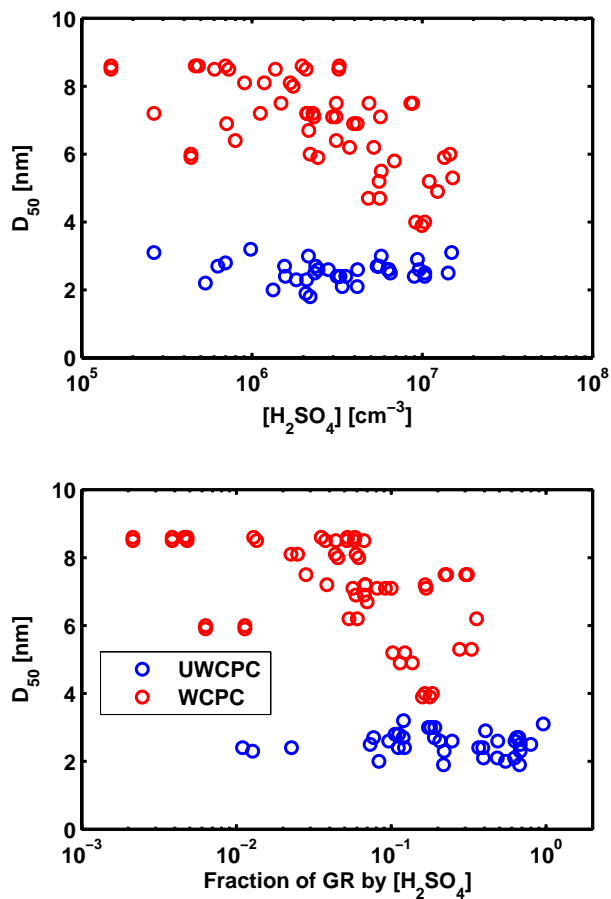


Fig. 10. The 50% cut-off sizes of the WPCP (red) and UWPCP (blue) as a function of modeled ambient sulfuric acid concentration (top) and the fraction of 3–7 (for WPCP) and 1.3–3 (for UWPCP) nm growth rates explained by sulfuric acid condensation (bottom).

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