The third Pallas Cloud Experiment: Consistency between the aerosol hygroscopic growth and CCN activity

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Measurements of aerosol chemical and hygroscopic properties and cloud condensation nuclei were carried out as a part of the third Pallas Cloud Experiment. In this study, the aerosol hygroscopicity parameter, κ, was determined using data from instruments operating in the sub-saturated and supersaturated water vapour regimes, as well as from measurements of aerosol chemical composition. During the campaign, κ varied from ~0.01 to ~0.37 as derived by Cloud Condensation Nuclei counter and Hygroscopic Tandem Differential Mobility analyser data, and from ~0.13 to ~0.60 as derived from Aerosol Mass Spectrometer data, the average values being 0.11 and 0.29, respectively. CCN closure calculations showed that the sub-saturated growth factor retrieved CCN concentration is lower than the measured one. Overall, at the Pallas site, aerosol hygroscopicity was size dependent with hygroscopicity increasing with size. Hence, size dependent information on composition is needed to predict CCN concentrations relevant to cloud droplet formation.

Introduction

An aerosol particle's response to a change in relative humidity (RH) is a function of its size and chemical composition. Soluble particles take up water and grow with increasing humidity, while particles composed of hydrophobic material take up only a small amount of water under normal ambient conditions. Aerosol particles become climatically important if they are able to grow to sizes of 50 nm and larger. Particles in this size range can act as cloud condensation

nuclei (CCN) and therefore may contribute to the indirect aerosol effect, a series of proposed impacts that include increased cloud albedo due to increases in cloud droplet concentrations (Twomey 1974, Albrecht 1989, IPCC 2007). Once particles grow to a size where they can become CCN, their ability to activate into cloud droplets depends on their chemical composition, and the water supersaturation of the surrounding air parcel, determined by the atmospheric conditions and aerosol size distribution (Seinfeld and Pandis 1998). Because both aerosols and clouds

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have a substantial influence on climate, the fundamental purpose in looking at aerosol–cloud interactions is to find a relation between the activating aerosol particles and the resulting cloud droplet population.

Aerosol hygroscopicity can be measured by several means. In sub-saturated conditions, aerosol hygroscopicity can be determined by, e.g. exposing a size-selected fraction of aerosols to water vapour of a known relative humidity (RH) (Rader and McMurry 1986). This RH is fairly easy to control, and it can range from 0 to ~95%. Particles will grow according to their hygroscopicity when exposed to this vapour; the ratio of the grown ("wet") diameter to the initial ("dry") diameter is defined as the hygroscopic growth factor. In supersaturated conditions (RH > 100%) aerosol hygroscopicity can be represented by a so-called critical diameter (D_c) of the aerosol, i.e. the average diameter needed for a particle to act as cloud condensation nuclei (also referred as D_{50}, the diameter corresponding to the 50% ratio of the activated particle to the total particle concentrations) at a certain supersaturation. Additionally, particle hygroscopicity can be estimated by measuring the composition of the particles. A simple parameter to represent hygroscopicity is the so-called kappa parameter (κ), varying between 0 for totally non-hygroscopic compounds to ~1.3 for highly hygroscopic NaCl (Petters and Kreidenweis 2007). Under atmospheric conditions it has been found that κ usually ranges from 0 to 1. Although the parameter is widely used, many discrepancies have been observed due to assumptions made in deriving the hygroscopicity parameter and heterogeneity of the aerosol population (Wex *et al.* 2009, Massoli *et al.* 2010, Pöschl 2011, Cerully *et al.* 2011).

In this manuscript, we present the results from the Third Pallas Cloud Experiment (PaCE-3) concerning aerosol hygroscopicity, their cloud-forming ability and chemical composition. The current study extends the work carried out during the first two PaCE campaigns (Lihavainen *et al.* 2008, Anttila *et al.* 2009, Kivekäs *et al.* 2009, Anttila *et al.* 2012). Anttila *et al.* (2012) also applied a model using κ-Köhler theory in order to compare the cloud droplet number concentrations with various aerosol properties and CCN concentrations. Also, estimates for the maximum supersaturation and updraft velocity reached in the observed clouds were provided, and the relative importance of the vertical velocity, particle size distribution as well as particle hygroscopicity to the cloud droplet number concentrations were assessed. Although the measurement campaign was organized to study aerosol properties during cloud events, this manuscript concentrates on a more general view of aerosol hygroscopic and CCN activation properties. For a more detailed analysis of the observed properties of clouds and their relation to the aerosol and CCN properties, *see* Anttila *et al.* (2012).

In this study, we scrutinize the behaviour of κ during the PaCE-3 campaign using water uptake measurements under sub-saturated and supersatured conditions, as well as aerosol composition data. At the measurement site the aerosol is strongly influenced by boreal and Arctic air masses, which, in this case, are both dominated by organic matter (e.g. Komppula *et al.* 2006). The combination of high organic mass fractions in particles and low particle concentrations makes the site an interesting place to test the accuracy of the hygroscopicity theories, since there have been very few studies conducted in similar conditions. In practice, the aim of the study was to compare κ values derived from various aerosol instruments. The instruments used will be described in detail in Methods. In addition, in our analysis of the data, we determined how the CCN closure calculations perform during this measurement period and whether they support the results given by previously-mentioned hygroscopicity calculations. The model used in the CCN closure calculations was first introduced in Anttila *et al.* (2009).

Methods

The Third Pallas Cloud Experiment, an intensive measurement campaign focusing on aerosol and cloud properties, was conducted by the Finnish Meteorological Institute and the University of Eastern Finland at the Pallas-Sodankylä Global Atmospheric Watch (GAW) station (Hatakka *et al.* 2003). This station consists of several

sites, but for this work we concentrate only on the two main measurement sites Sammaltunturi (67°58´N, 24°07´E, 560 m a.s.l.) and Matorova (68°00´N, 24°14´E, 340 m a.s.l.), in Muonio, Finland. The Sammaltunturi measurement site is located on top of a fell, which rises about 300 m above the surrounding area thus being a very suitable site for ground-based aerosol–cloud interaction measurements. The Matorova site lies about six kilometres northeast of Sammaltunturi. In this study, a 13-day (21 Sep.–4 Oct. 2009) set of data was analysed to investigate hygroscopicity and cloud-forming properties of aerosols in this remote continental site. All the instruments, except an Aerosol Mass Spectrometer (AMS; Aerodyne Research Inc., USA), were located in Sammaltunturi. The AMS was located at the Matorova site due to logistical constraints.

Instrumentation

A differential mobility particle sizer (DMPS) was used to measure the aerosol number size distribution. The DMPS consists of a 28-cm-long Hauke-type differential mobility analyser (DMA) (Winklmayr *et al.* 1991) with a closed loop sheath flow arrangement (Jokinen and Mäkelä 1997) and a condensation particle counter (CPC, TSI model 3010). Before sizing, the aerosol is neutralised with a 370-MBq Nickel-63 beta source. The instrument was operated as described by Komppula *et al.* (2005). The DMPS was attached to the total air inlet, which lets in all particles including cloud droplets. The cloud droplets evaporate in the inlet, and the dry cloud condensation nuclei were measured together with the non-activated particles. The DMPS measured the dry mobility diameter range 7–500 nm in 30 discrete size fractions. The whole size range was scanned in approximately five minutes.

The Cloud Condensation Nuclei Counter [CCNc, DMT model CCN-100, described by Roberts and Nenes (2005)] was operated at a total flow rate of 0.5 LPM and at five different supersaturations (SS = 0.2, 0.4, 0.6, 0.8 and 1.0%), each set for 15 min. Data processing included skipping the first five minutes of data after changing the SS value to ensure that the CCNc column was operating under stable con-

ditions. The total aerosol number concentration (CN) was measured with a condensation particle counter (CPC, TSI model 3772) connected to the same sampling line as CCNc, and the activated fraction was determined by dividing the concentration of activated droplets measured by CCNc by CN.

Particle hygroscopicity in the sub-saturated region was measured with a custom-built hygroscopicity tandem mobility analyser (HTDMA). The HTDMA was constructed at the Finnish Meteorological Institute, and consists of four main parts: "Dry" DMA for selecting the dry sizes; aerosol humidifier, which humidifies the sample air to wanted RH; "Wet" DMA, where the humidified aerosol is size-segregated; and a condensation particle counter (CPC, TSI model 3772), where humidified and size-segregated aerosol concentrations are measured. The sample air flow rate in the HTDMA is 1 LPM. Both DMAs work in a closed loop sheath air arrangement, with the "Dry" DMA's sheath flow set at 9 LPM and the "Wet" DMA's sheath flow set at 6 LPM. The aerosol is humidified solely in the sample air, using a heated Gore-Tex humidifier. The HTDMA was operated to measure the hygroscopic growth factor (GF) at a constant relative humidity (RH) of 90% at eight different dry diameters from 15 to 265nm. Both CCNc and HTDMA were attached to the total air inlet. A more detailed description of the system can be found in Anttila *et al.* (2012).

Aerosol chemical composition was measured using a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-Tof-AMS). AMS can provide information on size-resolved, non-refractory composition of submicron aerosols. Detailed descriptions of AMS measurements, calibration, modes of operation and data processing can be found in other publications (*see* Jayne *et al.* 2000, Allan *et al.* 2003, DeCarlo *et al.* 2006, Canagaratna *et al.* 2007). In this campaign, AMS was operated in a cycle of three modes every ten minutes: 2.5 min V-mode to obtain the mass concentrations of non-refractory species; 2.5 min PTOF (particle time-of-flight) mode to determine size distributions of species under the V-mode; and 5 min W-mode to obtain the high resolution mass spectral data. In addition, Black Carbon (BC) concentration was measured with

a Multi-Angle Absorption Photometer (MAAP, Thermo Scientific Model 5012). Both AMS and MAAP were attached to the total air inlet.

During the PaCE-3 campaign, measurements of the aerosol hygroscopic growth, CCN activity and composition were made and were used to derive κ (Petters and Kreidenweis 2007) using several different methods described in the following sections.

Aerosol water uptake: κ-Köhler theory

The κ-Köhler theory (Petters and Kreidenweis 2007) can be used to predict particle water content in the subsaturated ($S < 1$) regime, as well as to predict the conditions for cloud droplet activation. κ has an upper limit of ~1.3 for the most hygroscopic species typically found in the atmospheric aerosol (e.g. sodium chloride). Lower values of κ indicate less-hygroscopic, or less CCN-active, behaviour.

In this study, the κ-Köhler model is applied to the measured data. This model represents the relationship between water activities and the solution strength using a single parameter κ, as follows:

$$a_{w} = \left(1 + \kappa \frac{V_{s}}{V_{w}}\right)^{-1} \qquad (1)$$

where a_{w} is the water activity, V_{s} is the volume of solute and V_{w} is the volume of water, thereby capturing the compositional information. κ can be derived from measurements of a particle's water uptake or using a thermodynamic model when combined with a suitable expression for the Kelvin term. Petters and Kreidenweis (2007) suggest that the Kelvin term, K_{e}, can be represented as:

$$K_{e} = \exp\left(\frac{4\upsilon_{w}\sigma_{sol/v}}{RTD}\right) \approx \exp\left(\frac{4\sigma_{w}M_{w}}{RT\rho_{w}D}\right), \qquad (2)$$

where υ_{w} is the partial molar volume of water, $\sigma_{sol/v}$ is the surface tension of the solution droplet, σ_{w} is the surfaced tension of water, M_{w} is the molecular weight of water, R is the universal gas constant, T is the temperature, ρ_{w} is the density of water and D is the droplet diameter. The assumptions being made are that the surface tension is equal to that of pure water and that the

partial molar volume of water can be represented by the molar volume of water.

As κ is derived directly from measured or modelled data, by definition it will give an unambiguous result at the input conditions. The applicability of the κ parameter as a function of particle size and RH has been assessed for a wide variety of aerosols of known composition and generally gives coherent κ values ($\pm 20\%$) (Petters and Kreidenweis 2007, Kreidenweis *et al.* 2008). This also has been demonstrated in ambient aerosol measurements conducted in subartic and boreal sites (e.g. Cerully *et al.* 2011, Sihto *et al.* 2011, Kammermann *et al.* 2010, Juranyi *et al.* 2010, 2011). The κ-model offers a way to parameterize atmospheric CCN activity; for example it may be possible to describe hygroscopicity of large aerosol populations in terms of just a single κ (Andreae and Rosenfeld 2008). In this study, the variability of κ as a function of dry size over a range of sub-saturated RHs and at supersaturated conditions was determined. The ability of single κ values to represent water uptake during distinct meteorological periods in a remote clean environment was also assessed.

Deriving κ using CCNc and HTDMA

Since the CCNc measured the bulk aerosol with no size-selection, the critical diameter (D_{c}) was determined using the DMPS data. The total CCN concentration was compared with the DMPS-derived number concentrations that are integrated from each diameter bin to the largest measured particle diameter (which was 500 nm, for this study). When the integrated number concentration equals the total CCN concentration at a particular size bin, the critical diameter was estimated by interpolation between this and the previous size bin (*see*, e.g. Furutani *et al.* 2008). Given the critical diameter and the supersaturation, we can estimate the hygroscopicity parameter κ_{CCNc} with the following expression

$$\kappa_{CCN} = \frac{4A^{3}}{27D_{c}^{3}\ln^{2}S_{c}}, \quad A = \frac{4\sigma_{w}M_{w}}{RT\rho_{w}}, \qquad (3)$$

where D_{c} is the critical diameter and S_{c} is the supersaturation applied in the CCNc. In this derivation of κ_{CCNc} it is assumed that particles of

similar size are internally mixed. In our case, this assumption is valid, based on the HTDMA data and measurements location, where local aerosol sources causing external aerosol mixtures are lacking.

For the HTDMA data, a log-normal function was fitted to each humidified particle size distribution to parameterize the particle hygroscopic properties. The performance of the fit was evaluated and it was concluded that the data can be adequately described by a single log normal function. For each measured distribution, a mean hygroscopic growth factor (GF) and general standard deviation (GSD), indicative of the width of the distribution, was thereby obtained for each time interval and each dry particle size measured by the HTDMA. Once GFs are obtained, κ_{HTDMA} can be derived using the following expression

$$\kappa_{HTDMA} = \frac{GF^3 - 1}{RH} \exp\left(\frac{4\sigma_w M_w}{RT\rho_w D_d GF}\right) + 1 - GF^3, \quad (4)$$

where D_d is the dry diameter.

Predicting aerosol hygroscopicity using the AMS data

The Zdanovskii, Stokes, and Robinson (ZSR) approximation states that the hygroscopicity parameter κ, is the sum of contributions from each aerosol constituent

$$\kappa = \sum_j \kappa_j \varepsilon_j, \quad (5)$$

where κ_i and ε_i are the volume fraction and hygroscopicity parameter, respectively, of aerosol component j (Petters and Kreidenweis 2007). Based on AMS data, the components can include organic and inorganic salts calculated from the measured ion concentrations (e.g. Raatikainen *et al.* 2010). When there are no significant variations in the composition of the organic and inorganic fractions only the inorganic and organic fractions are needed for a reasonably good prediction (e.g. Cerully *et al.* 2011):

$$\kappa = \varepsilon_i \kappa_i + \varepsilon_0 \kappa_0, \quad (6)$$

where ε_i and ε_0, and κ_i and κ_0, are the volume

fraction and hygroscopicity parameters of inorganic and organic compounds, respectively. The relevant inorganic ions detected by AMS include ammonium, nitrate, and sulphate. In order to find the volume fraction, their mass concentrations were combined and, as ammonium sulphate and ammonium nitrate dominated the inorganic mass, the densities of ammonium sulphate, 1.769 g cm^{-3}, and ammonium nitrate, 1.725 g cm^{-3}, were assumed (Lance *et al.* 2009). The κ values used for ammonium sulphate and ammonium nitrate are 0.61 and 0.67, respectively. All of the other chemical compounds were treated as organic with a κ value of 0.1 (Petters and Kreidenweis 2007). The organic volume was calculated by assuming a particle density of 1.4 g cm^{-3} and the measured mass concentrations (Lance *et al.* 2009). In addition, black carbon (BC) concentration measured by a Multi-Angle Absorption Photometer (MAAP) was included in κ_{AMS} calculations with a κ value of zero.

CCN closure calculations

To further analyse the applicability of HTDMA-derived growth factors to predicting CCN concentrations at various supersaturations, we used a previously developed model described in detailed in Anttila *et al.* (2009, 2012). Briefly, the model calculates the total number of CCN-active particles at a supersaturation s, $CCN_{tot}(s)$, using the following equation:

$$CCN_{tot}(s) = \sum_{i=1}^{N} AF_i(s) CN_{tot,i}. \quad (7)$$

Here the summation is taken over DMPS size channels, and N is the number of the channels. Also, $AF_i(s)$ is the fraction of particles, having a dry size corresponding to the channel i, that are predicted to be activated at the supersaturation s, and $CN_{tot,i}$ is the total particle number concentration in the channel i. The functions AF_i are calculated using eq. 5 from Anttila *et al.* (2009). To summarize the process, power law functions are fitted to GFs and GSDs, obtained as described above, to extrapolate the results to the dry diameters measured with the DMPS. For each channel i in the DMPS, a mean hygroscopic growth factor (GF$_i$) and general standard devia-
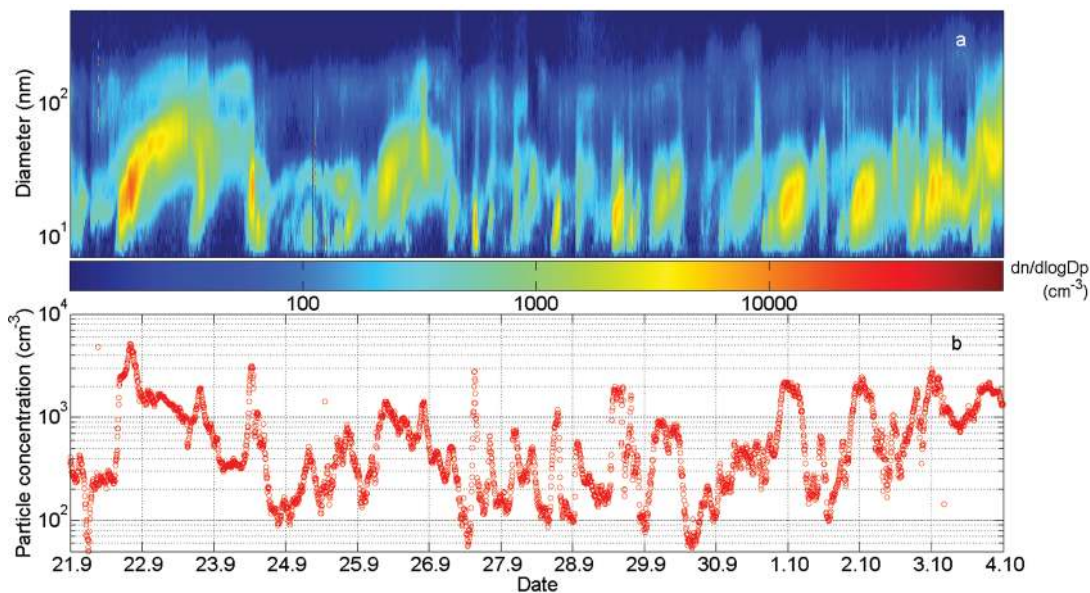
Fig. 1. (**a**) DMPS number size distribution and (**b**) number concentration for the study period.

tion (GSD_i) was thereby obtained. This allowed for calculating the distributions of hygroscopic growth factors for each size class i which were then converted to the corresponding distributions of critical supersaturations. By combining this with the particle size distributions measured with the DMPS, the CCN concentrations were calculated as well. Here GF distributions measured for different particle sizes were extrapolated to the size range covered by the DMPS to account for the particle mixing state and size dependence of particle hygroscopicity when total CCN concentrations in different supersaturations were calculated using the Köhler theory. In CCN calculations presented below, the temperature was set to 298 K and the particle surface tension was assumed to be that of water.

Results and discussion

Meteorological conditions, aerosol number, size and chemical composition

During the first half of the campaign the air masses arriving at Pallas came from the northern Atlantic. The second half of the campaign was characterized by air masses of the Arctic origin, even though sometimes the air had spent several days above land in northern Scandinavia. The ambient temperature at the Sammaltunturi site was on average 1.8 °C and varied from –4.8 °C to +9.2 °C during the campaign period. The winds were mostly westerly, with an average wind speed of 6.1 m s⁻¹. Aerosol number concentrations ranged from ~50 to 5000 cm⁻³, the average number concentration being around 700 cm⁻³ (median value 481 cm⁻³). A number of new particle formation events were observed (Fig. 1). In particular, a prominent event occurred during 21–22 Sep. 2009, when the growth of the newly-formed particles lasted for 24 hours and was followed by another formation event. This September event (on 21 Sep. 2009) is interesting with regard to the κ-analysis because of the high number and, in this case, increased mass concentrations of aerosol particles. DMPS mass was calculated by assuming a particle dry density of 1.5 g cm⁻³ and particle sphericity. Also the mass concentrations are very low at the Pallas GAW station (Fig. 2). Mass concentrations were < 1.2 μg m⁻³ during the whole campaign and the average total AMS mass loading was 0.26 μg m⁻³ (the median value of 0.16 μg m⁻³). On average, the AMS-measured aerosol mass was governed by organics (49%), followed by sulphate (27%), ammonia (15%) and nitrate (9%). The black carbon (BC) concentrations were small as compared with those
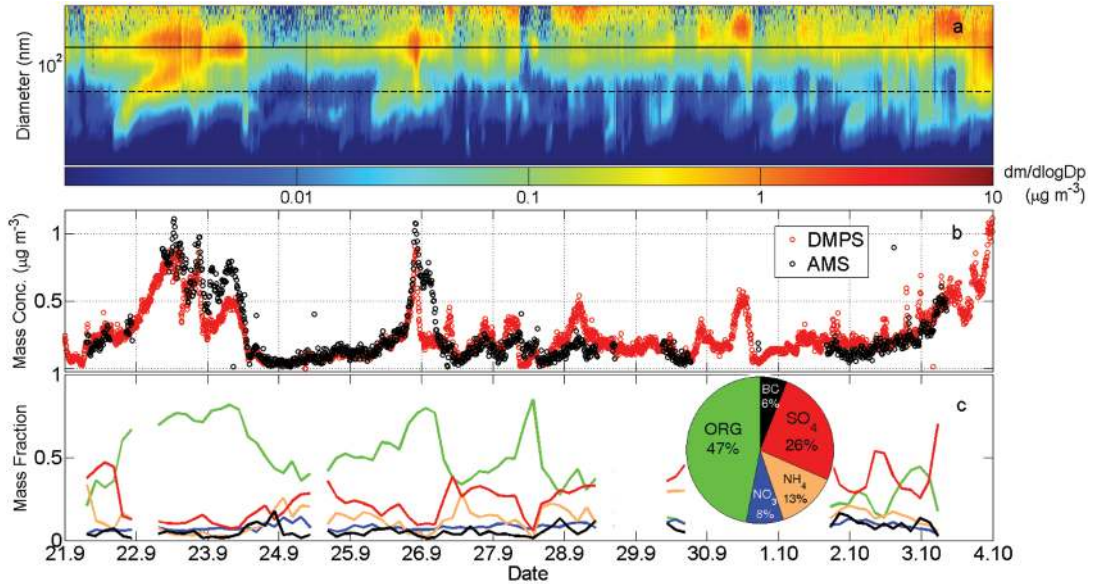
Fig, 2. (**a**) DMPS mass size distribution, with solid and dashed lines marking the HTDMA dry sizes D_d = 165 nm and D_d = 50 nm, respectively; (**b**) DMPS and AMS derived mass concentrations over the measurement period (a density of 1.5 g cm^{-3} was used in DMPS mass calculations). (**c**) AMS- and MAAP-derived mass fractions for organics (ORG), nitrate ion (NO$_3$), ammonium ion (NH$_4$), sulphate ion (SO$_4$) and black carbon (BC), the pie chart shows the campaign averaged fractions.

of other compounds. On average, the BC concentration measured by a Multi-Angle Absorption Photometer (MAAP) was about 6% of the total mass measured by AMS.

Aerosol hygroscopicity

CCNc-derived average critical diameter (D_c) values and HTDMA-measured growth factor (GF) values, together with κ values derived from both instruments, are given in Tables 1 and 2. It is worth noting that the quantity of data points in HTDMA dry sizes of 15 and 35 nm is low because of low particle concentration in this size

range and thus the reliability of these two data points is poor. The relation between the particle dry size and critical supersaturation, as well as the κ values, derived from CCNc follows the behaviour presented in the review paper by Kerminen *et al.* (2012) reporting κ values measured under various tropospheric conditions.

We compared CCNc to HTDMA observations at the following pairs of conditions: SS = 0.2% and D_d = 165 nm, respectively and SS = 1.0% and D_d = 50 nm, respectively (Fig. 3). This was done because, at these conditions, both instruments measured particles that were in the same size range, thus allowing the application

Table 1. Measured CCNc critical diameter (D_c) and κ values (campaign average ± SD).

SS(%)	D_c(nm)	κ
0.2	138 ± 20	0.19 ± 0.08
0.4	98 ± 16	0.13 ± 0.07
0.6	85 ± 15	0.09 ± 0.04
0.8	75 ± 15	0.08 ± 0.04
1.0	64 ± 11	0.08 ± 0.03

Table 2. Measured HTDMA growth factor (GF) and κ values (campaign average ± SD).

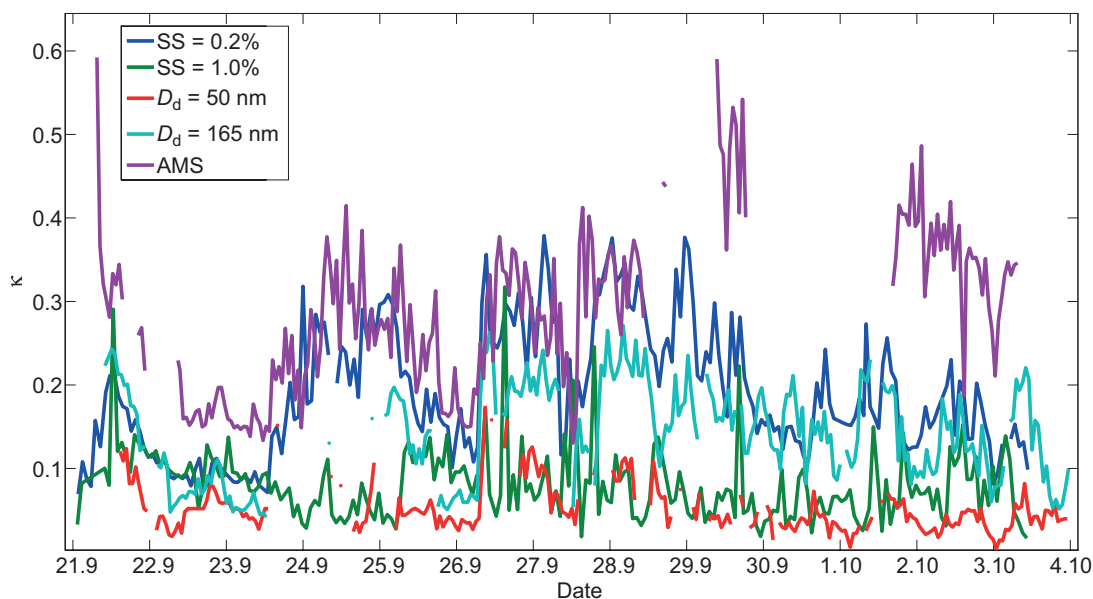| D_d(nm)	GF	κ
15	1.08 ± 0.05	0.07 ± 0.05
35	1.10 ± 0.05	0.06 ± 0.03
50	1.10 ± 0.06	0.05 ± 0.03
75	1.16 ± 0.10	0.08 ± 0.06
110	1.24 ± 0.11	0.12 ± 0.06
165	1.29 ± 0.14	0.14 ± 0.06
265	1.34 ± 0.13	0.17 ± 0.08

Fig. 3. κ derived from three different instruments, CCNc (SS = 0.2% and SS = 1.0%), HTDMA (Dry sizes D_d = 50 and 165 nm) and HR-AMS/MAAP.

of the κ-theory and the use of mass concentrations given by AMS over the same size range. Another criterion for selecting these pairs of D_d and SS was that the quantity of data points was the highest at these conditions. Since the AMS-derived κ value, in practice, is only a function of composition of the aerosol at any given time, it is also necessary to investigate the size range of the mass/volume distribution of the aerosol population before it is reasonable to compare κ_{AMS} with κ_{CCNc} and κ_{HTDMA}. During the campaign, the mass size distribution (and thus the volume size distribution) of the aerosol population peaks at the size range of well over 100 nm (Fig. 2a). Hence, it is not surprising that κ_{AMS} generally agrees best with the κ_{CCNc} (SS = 0.2%) and κ_{HTDMA} (D_d = 165 nm) values (Fig. 3). Only during the previously mentioned new particle formation event on 21–22 Sep. 2009, were all the κ values, except for κ_{AMS}, reasonably close to each other. This is probably mainly due to the following reasons: during new particle formation and the subsequent growth of the particles the organic mass fraction of the particles is very high and most likely the composition of different sized particles is similar due to internally mixed aerosol in the Aitken-mode size range. Because AMS determines mass fractions also for particles larger

than this range, the discrepancy between κ_{AMS} and other κ values can be explained. In addition, for most of the time, aerosol hygroscopicity is size-dependent so that larger particles are clearly more hygroscopic than the small ones, which is most likely due to fact that the solubility of organics is higher, and also the fraction of inorganics (e.g. sulphate) is larger with the bigger particle sizes. Thus, hygroscopicity derived from AMS overestimates the CCN potential of particles in the size range of 80–120 nm (Anttila *et al*. 2012), where the critical size for activation usually resides in the typical low level clouds at Pallas station. Unfortunately, the aerosol concentrations during the campaign were too low to see if size-resolved composition measurements would improve the agreement, as was done by Wu *et al*. (2013) under more polluted conditions. Juranyi *et al*. (2010, 2011) found a good agreement between measured and bulk composition-derived CCN concentrations in Jungfraujoch, where aerosol concentrations can be as low as in Pallas, but they found particle composition to be more size independent than in our case.

The best agreement between various κ values is found with the HTDMA and CCNc (Figs. 3 and 4). This is not surprising since the derivation of these two parameters is similar, and
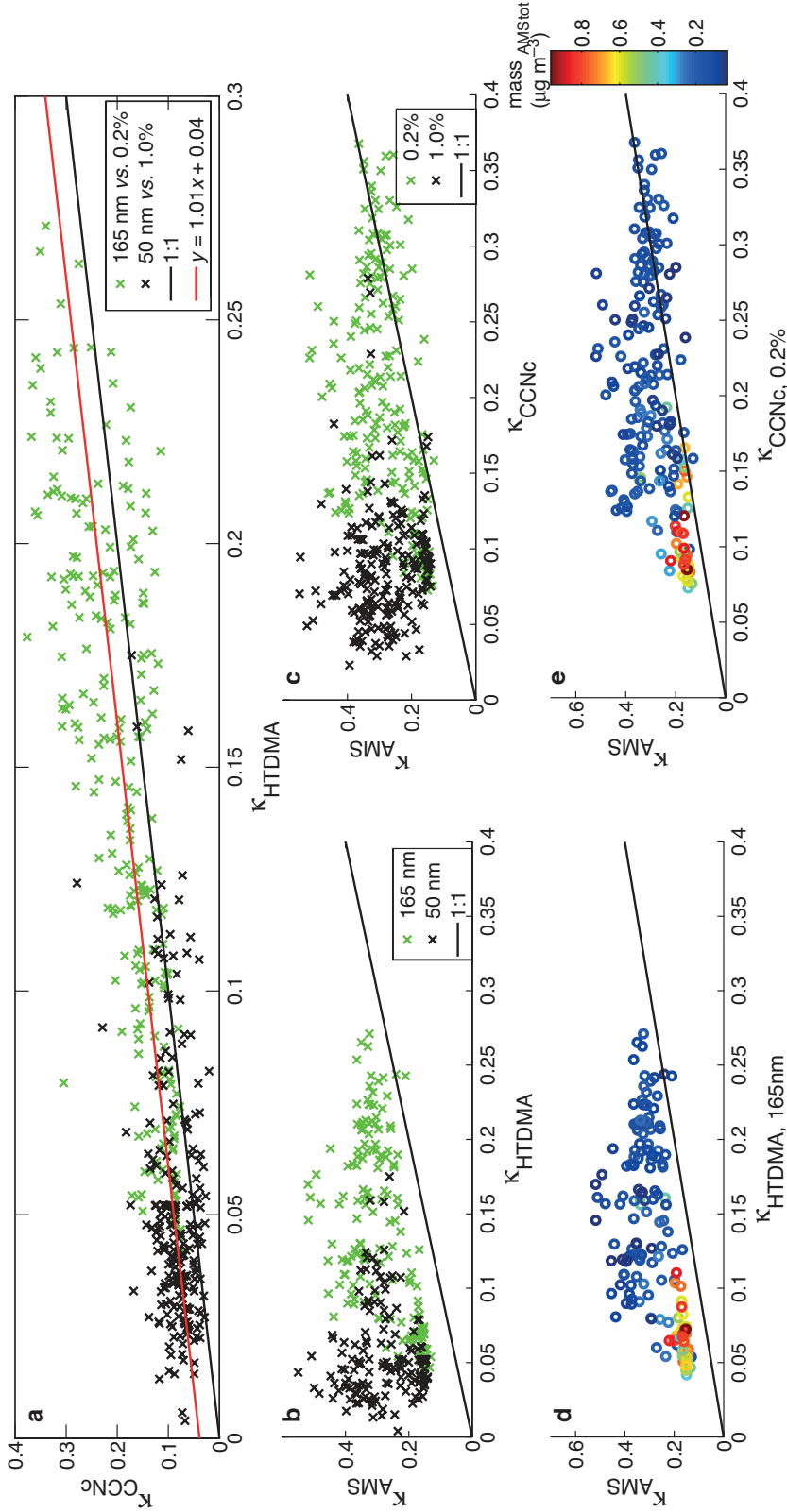
Fig. 4. The consistency between κ derived from different instruments. (**a**) The applicable pairs of κ values from HTDMA and AMS, and (**c**) CCNc and AMS, compared. (**d**) AMS κ compared with $\kappa_{HTDMA,165nm}$ and (**e**) with $\kappa_{CCNc,0.2\%}$; the colour indicates the total mass concentration measured by AMS. In all panels the solid black line is the 1:1 line and in panel **a** the solid red line is the optimal fit ($y = 1.01x + 0.04$) given by the least-squares method.

the D_d and SS pairs were chosen in such way that the instruments measured particles that were in the same size range. Overall, κ_{CCNc} tends to be higher than the HTDMA-derived κ (*see* Fig. 4a) with a difference of 0.04. This is a common trend found also in other studies (e.g. Good *et al*. 2009, Massoli *et al*. 2011). The comparison between κ_{HTDMA} and κ_{CCNc} gives an R value of 0.82. If the two different combinations of dry diameter and supersaturation are compared separately, R values are as follows: 0.74 (D_d = 165 nm *vs*. SS = 0.2%) and 0.29 (D_d = 50 nm *vs*. SS = 1.0%), with κ_{CCNc} being on average 0.03 higher than κ_{HTDMA}. This is in agreement with laboratory studies focusing on secondary organic aerosol which show higher κ values for CCNc than HTDMA (e.g. Massoli *et al*. 2010).

Comparison of κ_{AMS} with κ_{HTDMA} and κ_{CCNc} does not show a good agreement (Fig. 4b and c). For example, if only the data from 165 nm and SS = 0.2% are compared with the AMS data, the R values are 0.50 and 0.42, respectively. Several possible reasons can be given for the relatively weak agreement. First the sampling site is not the same: the distance between the sampling sites is 6 km and the difference in altitude is 220 m. However, it has been previously shown that the observed aerosol is representative for larger area (Komppula *et al*. 2003, 2005), and thus the average aerosol composition should be the same at both stations. Also, as the mass concentrations are low, the size-dependent composition cannot be determined from AMS. Thus the measured bulk composition can represent larger sizes than 165 nm during some parts of the campaign. The third reason could be overestimation of organic hygroscopicity. By setting κ for organics to zero, we would decrease κ_{AMS} on average by 0.04. However, the R values would practically remain the same.

CCN closure

As was discussed in the previous section, the agreement between HTDMA- and CCN-measured hygroscopicities is reasonable only for certain combinations of the dry particle sizes and supersaturation. However, the CCNc-derived hygroscopicities are generally higher as com-

pared with those obtained from the HTDMA data (Figs. 3 and 4). In order to further investigate differences between the results derived from these two instruments, we compared the measured CCN concentrations with those calculated using the model described above. In the base-case calculations, all the possible information from the performed HTDMA measurements, i.e. size and time resolved hygroscopic growth factors, are used as input. In the performed sensitivity studies, we also studied how the results change if mean hygroscopic growth factors, averaged over time and/or size, are used as input in the CCN calculations instead.

As a base case, we used size- and time-dependent measurements from the HTDMA and CCNc (Fig. 5a). The GF-retrieved CCN concentrations were lower than the measured concentrations, with a mean relative difference of 29.7%, and the mean GF-retrieved CCN concentration were 25.7% lower than the measured CCN concentration. The tendency to underpredict the measured CCN concentrations is consistent with lower values of HTDMA-derived κ values as compared with those obtained from the CCN measurements (*see* previous section). The average relative differences in the measured and predicted CCN concentrations were almost independent of supersaturation (*see* Table 3). On the other hand, the agreement between the measured and GF-retrieved CCN concentrations increased with an increasing saturation when measured by the variance of residual or by the degree of correlation (Table 3).

In the first sensitivity study, we averaged particle hygroscopicity over the size so that the values of $AF_i(s)$ in Eq. 7 were calculated using the same value of GF for all the channels i. This value was obtained by calculating the average value of GF_i over the size channels i for each time instant. Hence the time dependence of particle hygroscopicity was still accounted for in these calculations. In the second sensitivity study, the GFs were similarly averaged over the size, but the resulting time series was further averaged over time to obtain a single value for GF which was used in Eq. 7 for all the particle sizes and time instants (Fig. 5b and c).

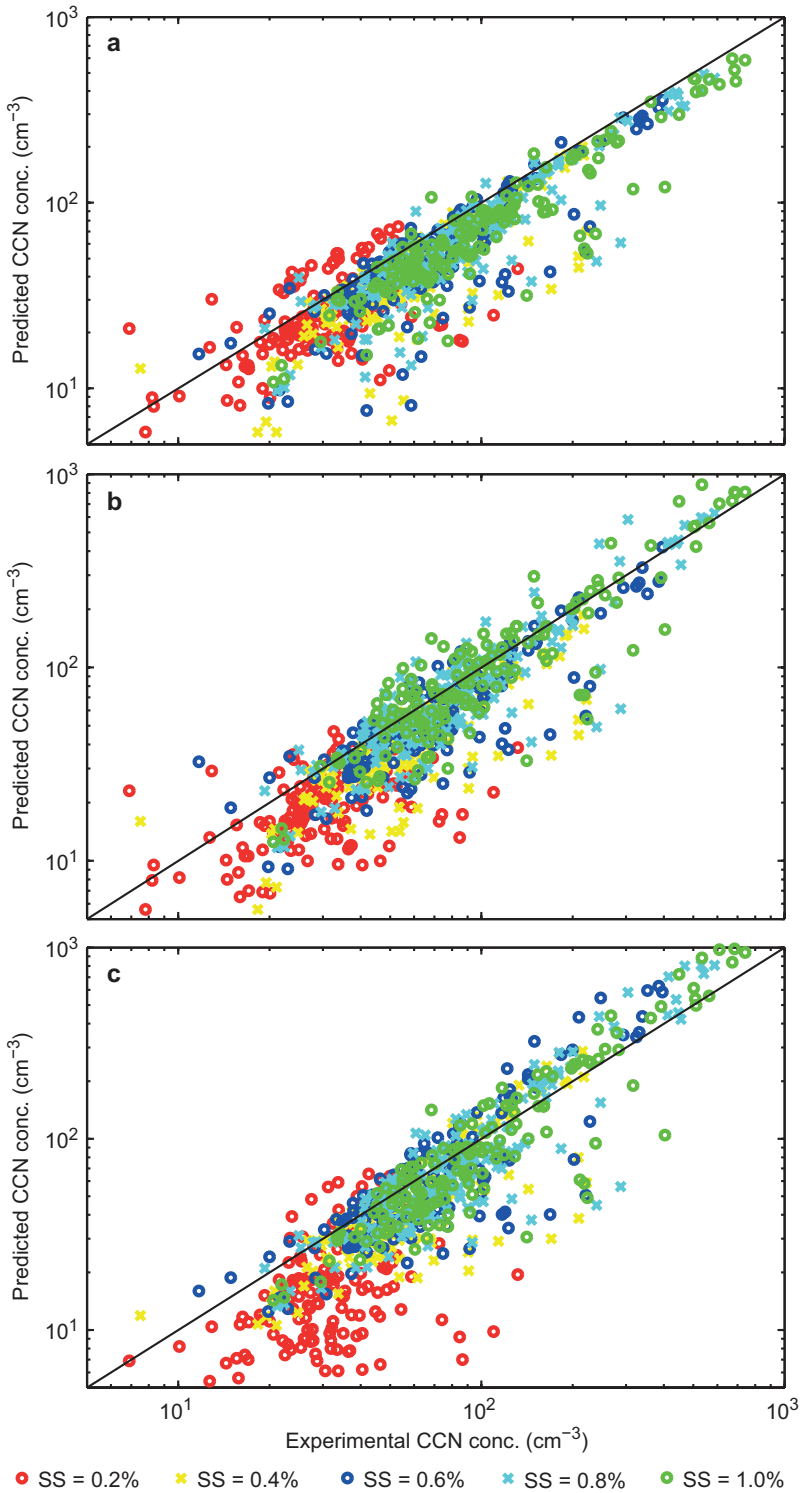In terms of the average relative error, the best agreement between measurements and calcula-

Fig. 5. A comparison between GF-retrieved and CCNc-measured CCN concentration with different supersaturations using (**a**) size and time dependent data, (**b**) size averaged and time dependent data, and (**c**) size and time averaged data from HTDMA and CCNc.

tions was reached when using the size-averaged hygroscopicities (SS = 0.2%) or when using a single parameter value to describe particle hygroscopicity (SS = 0.4, 0.6 and 0.8%). On the other

hand, the largest R values and lowest variances of the residuals were reached in the base case calculations, excluding the results for SS = 0.2% where the best correlation and lowest variance were found for the case with size-averaged, time-resolved hygroscopicities (Table 3). These somewhat counterintuitive results stem partly from the use of size-averaged hygroscopicity in the sensitivity studies. As a result of the averaging, hygroscopicity of small particles was generally overestimated and, *vice versa*, hygroscopicity of large particles was underestimated because particle hygroscopicity tended to increase with increasing size (Table 2). Threshold sizes needed for CCN activation shift to smaller diameters with increasing supersaturation and hence this resulted in better agreement at high supersaturation and weakened performance at the lowest supersaturation. Thus averaging the composition in CCN calculations is masking the difference seen in the hygroscopicities derived from different instruments and average relative difference between the measured and predicted CCN concentration is actually decreased although the correlation between predicted and measured concentration is worse. This is due to differences in the measured hygroscopicities between two instruments and thus averaging of data can lead to erroneous results even though CCN closure was improved.

Summary and conclusions

Concurrent measurements of aerosol chemical and hygroscopic properties and cloud condensation nuclei (CCN) were carried out as a part of the third Pallas Cloud Experiment, which took place at a remote measurement site located in northern Finland in autumn 2009. We focused on hygroscopic parameterisation and CCN closure calculations to investigate the applicability of the κ-Köhler theory and the relationship between modelled and measured CCN concentrations.

During the campaign, the station was influenced by Arctic air masses with total aerosol mass concentrations of around 1 μg m^{-3} and aerosol number concentrations between ~50 and 5000 cm^{-3}, with the average number concentration being around 700 cm^{-3}. On average, the AMS-measured aerosol mass was governed by organics (49%), followed by sulphate (27%), ammonia (15%) and nitrate (9%). The combination of high organic mass fractions in particles and low particle concentrations make the site an interesting place to test the authenticity of the hygroscopicity model theories, since there have been very few studies conducted in similar conditions.

The estimated κ values varied from ~0.01 to ~0.37 with the CCNc and HTDMA data, and from ~0.13 to ~0.60 with the AMS data, the average values being 0.11 and 0.29, respectively. Both HTDMA and CCNc data showed similar size dependence for κ with average values increasing from ~0.06 for 50 nm particles (0.08 for SS of 1.0%) to 0.17 for 265 nm particles (0.19 for SS of 0.2%). By choosing a supersaturation and dry diameter pair (D_d = 165 nm vs. SS = 0.2%) for closer scrutiny, the correlation between κ values determined from the CCNc and HTDMA data showed fairly good agreement ($R = 0.74$). However, the correlations with AMS-derived κ were weak (AMS *vs.* HTDMA at D_d = 165 nm: $R = 0.50$, and AMS *vs.* CCNc at SS

Table 3. The comparison between - retrieved and measured CCN concentrations. R is correlation, MD is mean difference and var(r) is variance of residuals.

SS(%)	Base case			Size averaged			Size and time averaged		
	R	MD(%)	var(r)	R	MD(%)	var(r)	R	MD(%)	var(r)
0.2	40.3	21.0	52.6	41.2	37.3	48.4	30.3	43.3	56.1
0.4	79.6	29.2	40.0	79.2	29.5	40.9	76.3	19.0	49.1
0.6	92.2	24.0	32.5	90.7	18.9	34.9	88.9	−3.1	68.0
0.8	95.3	24.3	31.9	92.3	5.9	42.6	93.2	−3.9	62.1
1.0	95.7	27.2	35.0	93.6	6.2	44.7	94.6	−4.6	57.6
Total	94.5	25.7	39.4	92.6	12.3	46.4	92.9	3.2	65.5

= 0.2%: R = 0.42). A good agreement between CCNc- and HTDMA-derived hygroscopicities was found especially during a strong new particle formation event, while κ_{AMS} was clearly greater. During the event, aerosol κ values were independent of particle size indicating similar composition over the measured size range, whereas during most of the time κ values were found to increase as a function of particle size. Thus, during most of the campaign the measured bulk aerosol composition resulted in high derived aerosol hygroscopicity for particle sizes relevant for cloud droplet formation. This is the main reason why, on average, the AMS-derived κ was larger than κ_{CCNc} and κ_{HTDMA}.

During the campaign, κ_{CCNc} was on average 28.4% higher than κ_{HTDMA}. This is in agreement with earlier studies showing similar deviation in values for organic dominating particles (e.g. Wex *et al.* 2009). CCN closure calculations showed that because of that difference, the GF-retrieved CCN concentration was lower than the measured one, with mean relative difference of 29.7% and mean GF-retrieved CCN concentration was 25.7% lower than the measured CCN concentration. Repeating the CCN closure calculations by averaging the GF data over size improved the CCN closure on average. The usage of a single composition for all particle sizes caused an overestimation of hygroscopicity for small particles and underestimation for large particles and this lead to an improved estimate of CCN concentration. However, this increased scatter between estimated and measured CCN concentrations, thus size resolved chemical composition should be used in the analysis whenever available.

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