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Measured and modelled Cloud Condensation Nuclei (CCN) concentration in São Paulo, Brazil: the importance of aerosol size-resolved chemical composition on CCN concentration prediction

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Abstract

Measurements of cloud condensation nuclei (CCN), aerosol size distribution and non-refractory chemical composition were performed from 16 to 31 October 2012 in the São Paulo Metropolitan Area (SPMA), Brazil. CCN measurements were performed at 0.2 %, 0.4 %, 0.6 %, 0.8 % and 1.0 % water supersaturation and were subsequently compared with Köhler theory, considering the chemical composition. Real-time chemical composition has been obtained deploying for the first time in SPMA an Aerosol Chemical Ionization Monitor (ACSM). CCN closure analyses were performed considering internal mixture.

Average aerosol composition during the studied period yielded 4.81 ± 3.05 , 3.26 ± 2.10 , 0.30 ± 0.27 , 0.52 ± 0.32 , 0.37 ± 0.21 and $0.04 \pm 0.04 \mu\text{g m}^{-3}$ for organics, BC, NH_4 , SO_4 , NO_3 and Cl, respectively. Particle number concentration was $12\,813 \pm 5350 \text{ cm}^{-3}$, being a large fraction in the nucleation mode. CCN concentrations were on average $1090 \pm 328 \text{ cm}^{-3}$ and $3570 \pm 1695 \text{ cm}^{-3}$ at $\text{SS} = 0.2\%$ and $\text{SS} = 1.0\%$, respectively.

Results show an increase in aerosol hygroscopicity in the afternoon as a result of aerosol photochemical processing, leading to an enhancement of both organic and inorganic secondary aerosols in the atmosphere, as well as an increase in aerosol average diameter.

Considering the bulk composition alone, CCN concentrations were substantially overpredicted ($29.6 \pm 45.1\%$ at 0.2 % supersaturation and $57.3 \pm 30.0\%$ at 1.0 % supersaturation). Overall, the impact of composition on the calculated N_{CCN} decreases with decreasing supersaturation, partially because using bulk composition introduces less bias for large diameters and lower critical supersaturations. Results suggest that the consideration of only inorganic fraction improves the calculated N_{CCN} .

Introducing a size-dependent chemical composition based on filter measurements from previous campaigns has considerably improved simulated values for N_{CCN} (average overprediction error $3.0 \pm 33.4\%$ at 0.20 % supersaturation and average under

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prediction error $2.4 \pm 20.5\%$ at 1.0 % supersaturation). This study provides the first insight on aerosol real-time composition and hygroscopicity on a site strongly impacted by emissions of a unique vehicular fleet due to the extensive biofuel usage.

1 Introduction

Cloud condensation nuclei (CCN) are a subset of atmospheric aerosol that enables the condensation of water vapour and formation of cloud droplets when submitted to a given level of water vapour supersaturation. The ability of a particle to act as a CCN depends strongly on its size distribution and chemical composition, which implies that the knowledge of both parameters would suffice to provide an accurate prediction on ambient CCN concentrations.

CCN are key elements of the hydrological cycle and climate on regional as well as global scales. Elevated concentrations of CCN tend to increase the concentration of cloud droplets in clouds and decrease its sizes, which may modify trends in rainfall (Khain, 2009 and references therein). In addition to their cloud microphysical effects, CCN also modulate cloud formation and convective behaviour through their radiative effects. One of the largest uncertainties in the current understanding of climate change is the response of cloud characteristics and precipitation processes to increasing aerosol concentrations. Therefore, one of the central challenges in climate assessment is to accurately describe the spatial distribution of CCN, its relative contribution from anthropogenic activities, and the dependence of CCN efficiency on the aerosol size distribution and chemical composition under atmospheric conditions (e.g. McFiggans et al., 2006; IAPSAG, 2007; IPCC, 2007; Andreae and Rosenfeld, 2008).

Currently there is no consensus on how much detail on aerosol mixing state and chemical composition is needed to predict N_{CCN} , which is expected to vary among aerosol types and with the aging of atmospheric aerosols. Nevertheless, CCN concentration was found to be predicted with relative accuracy assuming simplified composition and an internal mixture in some studies (e.g. Liu et al., 1996; Cantrell et al., 2001;

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Roberts et al., 2002; VanReken et al., 2003; Rissler et al., 2004; Conant et al., 2004; Gasparini et al., 2006; Broekhuizen et al., 2006; Ervens et al., 2007; Chang et al., 2007; Andreae and Rosenfeld 2008; Wang et al., 2008; Gunthe et al., 2009; Shinozuka et al., 2009). Given the complex mixtures of aerosol composition, with both inorganic and organic components, and the composition dependency on aerosol size, a complete and rigorous description of aerosol composition, mixing state and also their ability to act a CCN a difficult task. As a result, the representation of aerosol composition and mixing state in large scale models are often greatly simplified. A common approximation, for example, is to consider aerosols to be an internally mixed, i.e., particles of any size are a mixture of all participating species and have the identical composition. Nevertheless, such simplified aerosol representation on atmospheric models can be significantly improved using an efficient parameterization for the calculated N_{CCN} given the current measurements techniques.

Megacities and large city-clusters are major source regions of atmospheric particulate matter and its precursors, with regional and global impacts (Gurjar et al., 2008). In recent years a number of studies were performed aiming to characterize the CCN properties of the aerosol particles in urban environments and their effects on regional air quality and climate (e.g. Matsumoto et al., 1997; Yum et al., 2005, 2007; Broekhuizen et al., 2006; Kuwata et al., 2007, 2008, 2009; Wiedensohler et al., 2009; Rose et al., 2010, 2011; Kuhn et al., 2010; Gunthe et al., 2011; Lance et al., 2013; Mei et al., 2013).

Aiming to constrain aerosol sources, processing and its impact on climate and human health in the São Paulo Metropolitan Area (SPMA), the project NUANCE-SP (*Narrowing the Uncertainties in Aerosol and Climate changeEs in the state of São Paulo*) has been designed. With 20 million people and over 7 million vehicles using a blending of gasoline with anhydrous ethanol (gasohol), pure ethanol, or diesel with biodiesel, the SPMA is one of the largest urbanized regions on the planet. Furthermore, the region is often impacted by industrial emissions (Albuquerque et al., 2012), thus resulting in a complex suite of sources of aerosols and its precursors. Within the scope of the

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NUANCE-SP project, aerosol and traces gases measurements were performed during winter and spring of 2012 within the city of São Paulo.

In this study we report the first CCN measurements performed within the SPMA. Furthermore, supporting measurements including real-time non-refractory chemical speciation, aerosol size distribution and Black Carbon (BC) concentration were performed. A comparison of modelled and observed N_{CCN} considering size resolved chemical composition based on filter measurements from previous campaigns has been performed as well.

2 Experimental

2.1 Measuring site and meteorological conditions

The SPMA is located at 23.5° S and 46.6° W, in the southeastern portion of Brazil and consists of 39 highly urbanized and industrialized towns, among which is included the city of São Paulo (Sánchez-Ccoyllo and Andrade, 2002). The urban site is almost entirely located in the Sedimentary Basin of Tietê River, oriented from east to west, with a mean elevation of 720 m a.s.l. on an extensive floodplain. This basin is bordered to the north by the Cantareira Hills, also oriented east to west and with altitudes reaching up to 1200 m. At the south-east side the valley is delimited by Serra do Mar with altitudes generally exceeding 800 m. SPMA is approximately 45 km from the Atlantic Ocean, holds about 0.1 % of the Brazilian territory and is the fourth largest urban conglomeration in the world. The climate is subtropical with dry winters and wet summers (Oliveira et al., 2003). The measurements were made at the Armando Salles de Oliveira campus of the University of São Paulo. The campus area is a vast park, with an area of 7.4 km², without strong local sources. Thus, air masses arriving at the station should be well mixed and make the measurements representative of the ambient pollution burden of the city.

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it is not observed a strong correlation between CN and N_{CCN} peaks throughout the sampling period.

During the whole period the integrated number concentration varied between 3000 cm^{-3} and $27\,174 \text{ cm}^{-3}$, with a mean aerosol concentration of $12\,813 \pm 5\,350 \text{ cm}^{-3}$ (Fig. 3c). Figure 3d shows the time series of aerosol mean diameter and volume, yielding an average value of 58 nm for the former and 117 nm for the latter. The mean aerosol number concentration attained a maximum values at noon, but has a secondary peak at 18:00 LT, as a function of traffic emissions (Fig. 3e). During observations a substantial fraction of the aerosols was present below $\sim 40 \text{ nm}$ as was measured by the DMPS.

The OPC measurements show that the number concentration of particles above 500 nm was small compared to the number concentration of CCN, even at $\text{SS} = 0.20 \%$.

The bulk mass concentrations of ammonium, sulphate, nitrate and organics as measured by the ACSM, are shown in Fig. 4a, along with the BC mass concentrations measured by the MAAP. Results are shown as 1 h average. Substantial variation on chemical composition was observed in the time-averaged ACMS data. The balance of ammonium, nitrate and sulphate concentrations revealed that the aerosol was far from being completely neutralized in many moments, especially during the morning, which indicate that aerosol are relatively acidic and considerably amount of sulphate can be in the form of ammonium bisulphate, as was also observed by Quinn et al. (2006) and Middlebrook et al. (2012). During other time intervals, the amount of NH_4 was above the amount needed for completely neutralization, and sulphate are probably present as ammonium sulfate, as is shown on Fig. 4b.

Figure 4c shows the mass fractions of the chemical components, listed in Table 2. The most abundant observed species were organics and BC, with a combined 86% of all mass (49.3% and 36.9% for organics and BC, respectively), indicating the relevant impact of diesel (heavy-duty) fuelled vehicle during the studied period. Other species contributed with 5.6%, 4.3%, 3.4% and 0.4%, for SO_4 , NO_3 , NH_4 and Cl, respectively. The relative contributions of Cl, NH_4 , NO_3 and SO_4 to the total mass frac-

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tion is relatively small (less than 14% on average) but changes significantly during the days (by a factor of 4) of the measurement period. The contribution of organics and BC to the total mass fraction is much larger than that observed by that of inorganics, according to previous studies in the area (Ynoue and Andrade, 2004), and BC is the one that presents the larger variability. The mean hourly concentration of inorganics seems to not have a remarkable variation during the day. The organic mass, nevertheless presents a large variation during the day. The minimum values are observed at 08:00 LT, while the maximum values are observed at 14:00 LT, as is shown in Fig. 4d, in relatively agreement with aerosol concentration observed in Fig. 3e. The lower concentration value for the organic fraction in aerosols seems to occur 1 h later than those observed to the aerosols number concentration. This is probably because the traffic emission results in nucleation of aerosols in diameters lower than 40 nm, which are not measured by the ACSM or low concentration of secondary organic aerosol. The mean concentration observed during the whole period are 4.81 ± 3.05 , 3.26 ± 2.10 , 0.30 ± 0.27 , 0.52 ± 0.32 , 0.37 ± 0.21 and $0.04 \pm 0.04 \mu\text{g m}^{-3}$ for organics, BC, NH_4 , SO_4 , NO_3 and Cl, respectively.

3.2 CCN modelling study and the sensitivity of calculated N_{CCN} to assumed aerosol size dependence composition

A particle's ability to act as CCN depends on its size and chemical composition. In this study both particle number size distribution and chemical bulk composition data are available. As such, supposing internal mixture of the species provided by ACSM and a simplified Köhler theory, we determine the critical supersaturation a dry diameter needs to be submitted to be activated. Köhler theory (Köhler, 1936; McFiggans et al., 2006) describes the equilibrium saturation ratio, S , over an aqueous solution droplet. According to Köhler theory S is defined by the ratio of p , the partial vapour pressure,

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composition on calculated N_{CCN} decreases with decreasing supersaturation, partially because using bulk composition introduces less bias for larger sizes at lower supersaturations, and also by the fact that aerosol mass determined by the ACSM is most defined by the largest particles. In this case, the fraction of inorganics and organics mass in larger aerosol approach that measured by ACSM.

It can also be shown that if a smaller solubility factor ($\kappa \sim 0.60$) is taken in to account for the inorganic fraction, the modelled overestimation values are only slightly smaller (less than 5 %) than those shown in Table 3a.

For the assumptions of size-averaged the small particles smaller than 40 nm do not affect the calculated CCN number concentration because $D_{0,\text{crit}}$ at the 1.0 % supersaturation was always above 40 nm.

A series of new simulations were performed varying the values of κ_{org} from 0.1 until 0.0, still considering internal mixing. The resulting overestimation becomes lower and lower as long as κ_{org} decrease from 0.1 until 0.0. The slope of fitted lines decreased to 1.11 and 1.40 for 0.2 % and 1.0 % supersaturation, respectively, when κ_{org} is set 0. There is also an decrease on the mean relation between modelled and observed N_{CCN} . Values decreased to 1.04 ± 0.36 and 1.41 ± 0.27 for 0.2 % and 1.0 % supersaturation, respectively.

3.2.2 Internal mixture and size dependent chemical composition

The implication of aerosol size chemical dependency on modelling of N_{CCN} are investigated using data from previous measurements campaign performed in São Paulo using a Micro-Orifice Uniform Deposit Impactor (MOUDI) and particle-induced X-ray emission (PIXE) analysis at the 2.4 MeV tandem Pelletron accelerator located in the Laboratory for Ion Beam Analysis of Materials at the University of São Paulo, as described in Albuquerque et al. (2012) and Sánchez-Ccoyllo and Andrade (2002). These studies have shown a size dependency of inorganic matter in Sao Paulo. The work of Vasconcellos et al. (2011), for instance, have shown that sulphate, nitrate, ammonium, calcium and sodium are the most abundant water-soluble ions in São Paulo. Figure 6 illustrate

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the 24 h mean mass distribution observed from 15 August to 5 September 2012, along with the sulphate distribution for the same period. Figure 6b depicts the fraction of sulfate to the total aerosol mass. It is clearly seen that sulphate is a major component of the accumulation mode (diameters larger than 180 nm), but values are largely variable. For small diameters (below 100 nm) the fraction of sulphate decreases systematically, and reaches a fraction of about 2.5 % at 20 nm. Considering the large fraction of sulphate on the accumulation mode and the large fraction of organic compounds on total aerosol mass, one can argue that organic compound is predominant at smaller particles. One can also conclude that particles in the nucleation or Aitken size range were composed mostly of organics.

The time resolved mass fractions defined above can now be used to feed the equation for κ considering a variation with size as a function of time. Again we use $\kappa_{\text{inor}} = 0.7$.

Considering that mass distribution observed by Aerosol Mass Spectrometer (AMS) was shown to be consistent with measurements by MOUDI data (Zhang et al., 2005), we assume that inorganic size fraction takes the same size dependency as observed for sulphate during measurements taken from 15 August to 5 September 2012, which are also close to those values observed on previous measurements campaigns. It is worth to say that CCN closure utilizing AMS measurements tend to be more successful (typically within 20–50 %), due to its fast time resolution (1 Hz) and ability to resolve size-dependent composition. CCN closure in remote environments that use filter-based methods have nevertheless given good closure, on the order of a few percent (Bougiatioti et al., 2009, 2011).

The new modelled results are presented on Fig. 7. The results of the size-dependent simulations are shown in Table 3b. Result show that when we use the inorganic fraction furnished by MOUDI+PIXE analysis there is a reduction on the slope of fitted lines for the comparison of modelled and observed N_{CCN} for all supersaturation. For 0.2 % supersaturation, for example, the slope is 1.09, with $R^2 = 0.41$, indicates a better agreement than when the mean values furnished by ACSM is considered on the simulation. It is also observed a reduction on the mean relation between modelled and observed

CCN, given now by 1.03 ± 0.33 . There is a reduction on the slope for all fitted lines relating simulated and observed N_{CCN} . For the case of 1.0 % supersaturation, the slope of fitted line is 0.98 with $R^2 = 0.77$, with mean relation between modelled and observed CCN of 0.98 ± 0.21 . For this particular assumption, $D_{0,\text{crit}}$ at the 1.0 % supersaturation was most of the time above 66 nm, with mean value of 67 nm.

Considering any k_{org} different from 0.0 imply increasing overestimation of N_{CCN} for all supersaturation. The overestimation, obviously, increases systematically for increasing supersaturation

These results shows that the measured number distribution of the DMPS, combined with the chemical composition information provided by the ACSM and the mean chemical fraction information of the MOUDI+PIXE analysis, provides a reliable estimate of CCN spectra.

3.2.3 Further improvement on the estimation of N_{CCN}

As previously stated, CCN closure utilizing AMS measurements tend to be more successful due to its fast time resolution and ability to resolve size-dependent composition. The use of mean values of MOUDI data although can significantly improve the estimation of N_{CCN} induce systematic bias as a function time of the day for all supersaturation. The results are shown in Fig. 8 where we can see the mean relation between modelled and measured N_{CCN} as a function of the time of the day. From 07:00 to noon LT, for example, the N_{CCN} modelled clearly tends to increase regarding observation, while an opposing tendency occurs during the afternoon. It can be concluded that the mean mass partition presented by MOUDI analysis underestimates the soluble fraction during the morning and overestimates it during the afternoon. Castanho and Artaxo (2001) found that 40 % of Fine particles were explained by Organic Carbon and Ynoue and Andrade (2004) found for data collected in 1999 that OC explained 25 % during the day and 43 % at night of fine particles. Considering that previous analysis have shown that the inorganic fraction tends to be higher during the day then during the evening in São Paulo, only a higher resolution (~ 6 h) MOUDI analysis could probably allow the study

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and parameterization of the aerosol soluble fraction as a function of the size and time of day.

4 Conclusions

Aerosol measurements in São Paulo city showed that the urban area is a strong source of aerosol particles. These particles can act as CCN and show large variability, presenting peaks that alternate with low N_{CCN} values. Minimum and maximum observed CCN number concentrations at a certain SS differed by a factor of four to one and suggest that chemistry composition is the main factor controlling the fraction of aerosols that can act as CCN.

The hygroscopicity range was substantially lower than that proposed for continental sites (Andreae and Rosenfeld, 2008), likely due to the higher volume fraction of organics. It was also observed that traffic emissions modulate the charge of aerosols, organic fraction and CCN efficiency.

The impact of k_{org} on calculated N_{CCN} concentration was examined calculating N_{CCN} for different k_{org} values (0.1, 0.07, 0.05, 0.03 and 0.00). Particle hygroscopicity was computed from the bulk composition (i.e., derived from ACSM measurements) using Eq. (3). Based on the particle hygroscopicity and κ -Köhler theory, the critical supersaturation was derived for each particle dry diameter (D_0). The N_{CCN} at the five supersaturations were then computed from D_0 and the measured dry particle size distributions. Results suggest that taking organic fraction in to account on the particles hygroscopicities only increases the overestimation of modelled N_{CCN} regarding observations.

Results show an increase in aerosol hygroscopicity in the afternoon as a result of aerosol photochemical processing, leading to an enhancement of both organic and inorganic secondary aerosols in the atmosphere, as well as an increase in aerosol average diameter.

Our study suggests that the prediction of N_{CCN} can be achieved with an error of about ± 22 % considering a mean size-dependent soluble fraction based on MOUDI+PIXE

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Table 2. Mean concentration (\pm standard deviation) for Organics, NH_4 , Sulfate, Nitrate, Chloride and Black Carbon concentration (in $\mu\text{g m}^{-3}$) measured in São Paulo from 16 to 31 October 2012.

Org	NH_4	SO_4	NO_3	Cl	BC
4.81 ± 3.05	0.30 ± 0.27	0.52 ± 0.32	0.37 ± 0.21	0.04 ± 0.04	3.26 ± 2.10

32379

Table 3. (a) Details on the predicted vs. measured N_{CCN} considering chemical composition measured by ACSM. a is the slope of the fitted line, R^2 is the square of the correlation coefficient.

Supersaturation (%)	a [-]	R^2 [-]	Mean predicted/measured N_{CCN} (\pm standard deviation)
0.20	1.38	0.39	1.30 ± 0.45
0.40	1.36	0.72	1.36 ± 0.32
0.60	1.46	0.78	1.47 ± 0.31
0.80	1.54	0.81	1.54 ± 0.31
1.00	1.56	0.81	1.57 ± 0.30

32380

Table 3. (b) Details on the predicted vs. measured N_{CCN} considering mean chemical size dependency furnished by MOUDI+PIXE and ACSM hourly chemical composition.

Supersaturation (%)	a [-]	R^2 [-]	Mean predicted/measured N_{CCN} (\pm standard deviation)
0.20	1.09	0.41	1.03 ± 0.33
0.40	0.93	0.68	0.95 ± 0.23
0.60	0.96	0.75	0.96 ± 0.22
0.80	0.98	0.78	0.98 ± 0.21
1.00	0.98	0.77	0.98 ± 0.21

32381

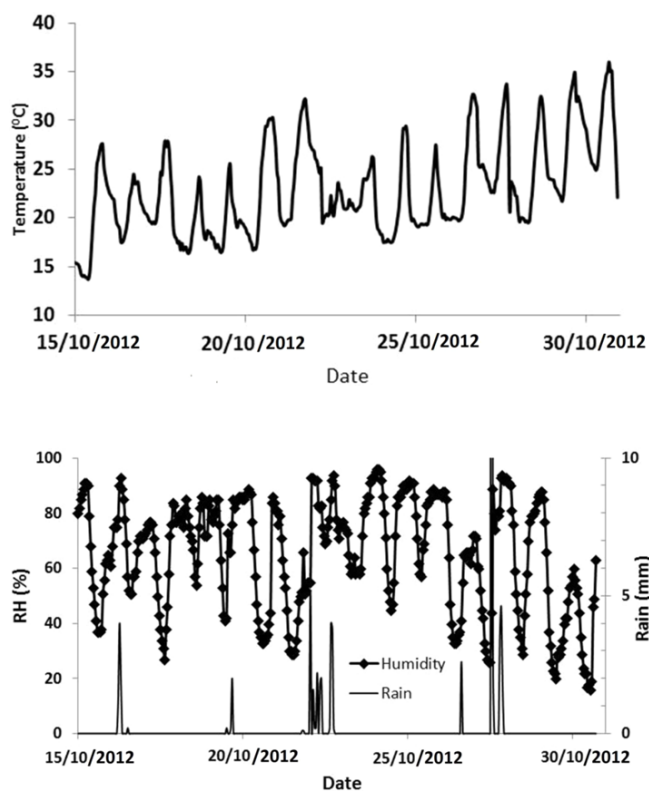


Fig. 1. Diurnal variation of the (a) temperature and (b) RH at the sampling site during the studied period.

32382

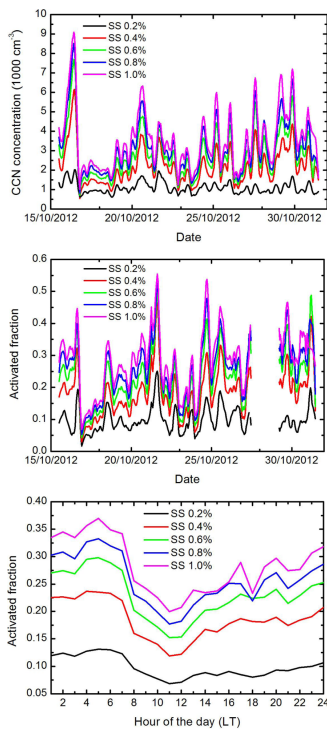


Fig. 2. Time series of (a) CCN number concentration, (b) the activated fraction (#CCN/N10-500) and (c) the mean hourly averaged over the whole period. The different colours represent the different supersaturations (SS).

32383

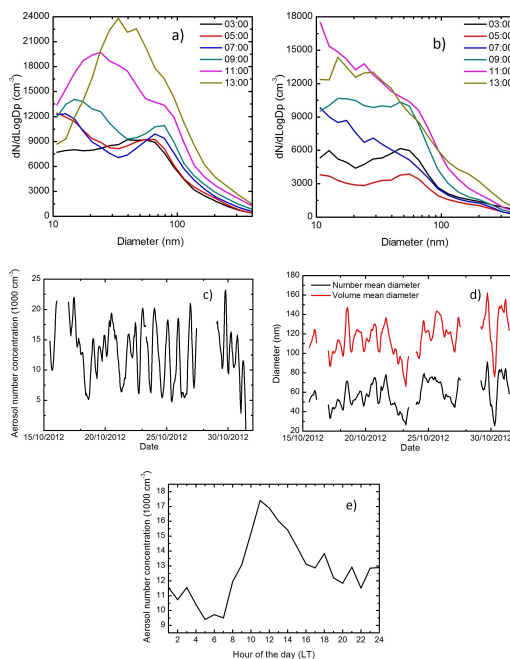


Fig. 3. (a) aerosol size distribution during 16 October 2012 in SP (b) the same as in (a), but for 17 October (c) Total aerosols concentration from 10 nm to 500 nm (d) mean aerosol diameter and mean aerosol volumetric diameter, and (e) Mean hourly aerosol total concentration.

32384

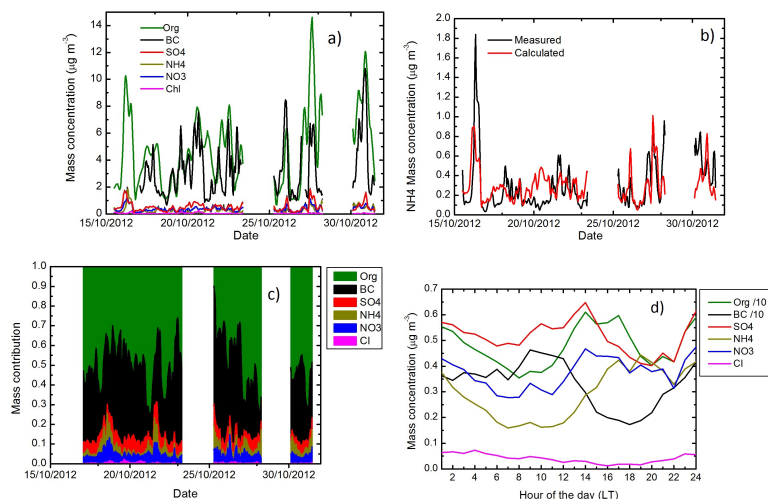


Fig. 4. Chemical composition of the aerosol, measured by the ACMS and the MAAP. **(a)** mass concentration of the individual species, **(b)** mass concentration of the measured NH_4 and the calculated amount needed for complete neutralization, **(c)** the mass fractions of the organics, NH_4 , NO_3 , SO_4 and black carbon, and **(d)** the mean aerosol chemical composition as a function of local time.

32385

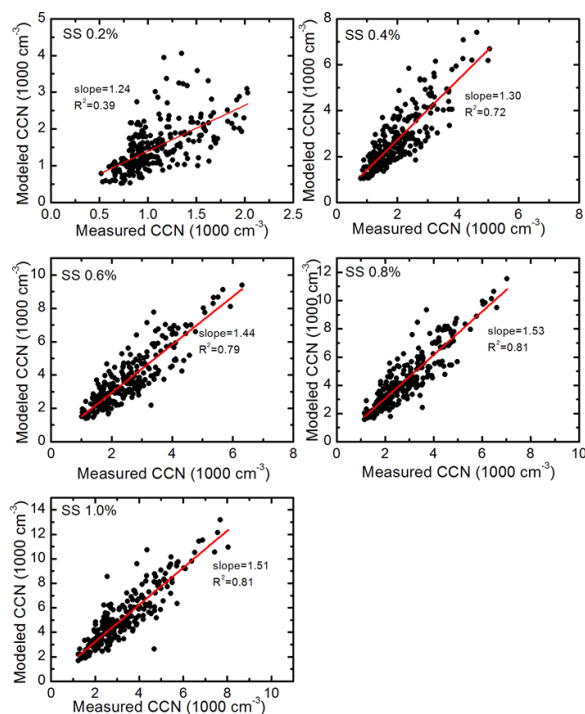


Fig. 5. Comparison of modelled and measured CCN concentrations using internal mixing for the 5 measured supersaturation (0.2%, 0.4%, 0.6%, 0.8%, and 1.0% SS).

32386

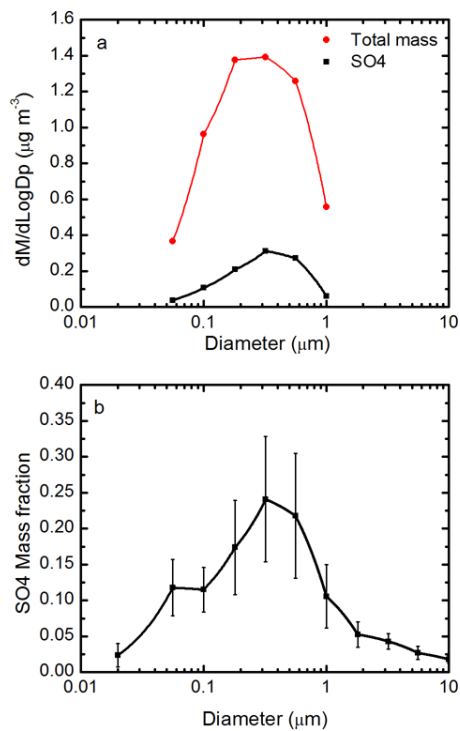


Fig. 6. Mean value of (a) $dM/d\log d$ ($\mu\text{g m}^{-3}$) for the period of 15 August to 5 September 2012 and (b) SO_4 mass fraction for the same period.

32387

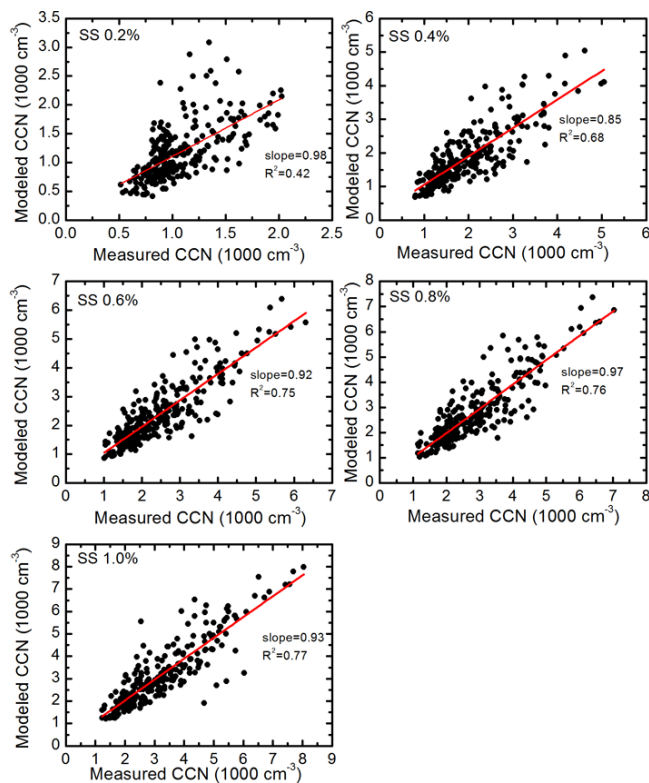


Fig. 7. Same as Fig. 5, but using the size dependence based on MOUDI+PIXE analysis.

32388

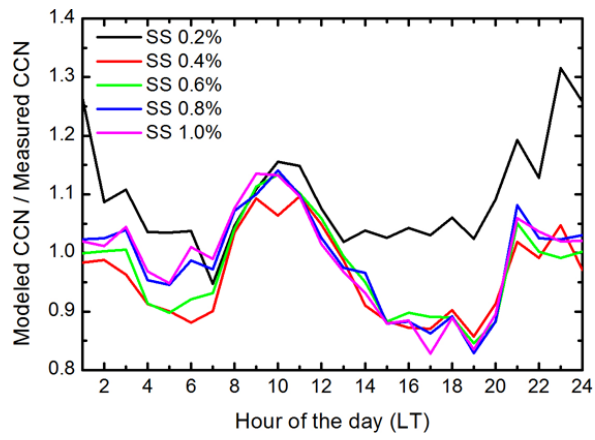


Fig. 8. Mean value of modelled N_{CCN} /Observed N_{CCN} as a function of local time.