



Measured and modelled Cloud
Condensation Nuclei
(CCN) concentration

G. P. Almeida et al.

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

G. P. Almeida¹, J. Brito², C. A. Morales³, M. F. Andrade³, and P. Artaxo²

¹Department of Physics, State university of Ceará, Fortaleza, Brazil

²Department of Applied Physics, Institute of Physics, University of São Paulo, Sao Paulo, Brazil

³Department of Atmospheric Sciences, Institute of Astronomy, Geophysics and Atmospheric Sciences, University of São Paulo, Sao Paulo, Brazil

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Received: 19 October 2013 – Accepted: 24 October 2013 – Published: 10 December 2013

Correspondence to: G. P. Almeida (gerson.almeida@uece.br)

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

ACPD

13, 32353–32389, 2013

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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;

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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.

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The instrumentation was set-up at the rooftop of the Pelletron particle beams accelerator building, in the Physics institute of the University of São Paulo. The top of the tower is about 40 m above mean ground level. Three vertical sampling lines with $\text{PM}_{2.5}$ inlets mounted 1 m above the roof provided sample air to the instruments. The sampling lines to the instruments were 3/8 inch stainless steel tubing with an inner diameter of 1/4 inch from the inlet to the instruments and 2.2 m in length. Each sampling line was exclusive for BC, chemical speciation, and size distribution (as well as CCN) measurements. Besides the instrumentation for aerosol characterization, a meteorological station (Lufft GmbH, model Ventus-200A) has been deployed as well. During the study the weather was sunny with occasional precipitation. The average air temperature and relative humidity (RH) for the whole period was 23.0 °C and 69 %, varying from 13.9 to 36.0 °C and from 96 down to 19 %, respectively (Fig. 1). During the period a moderately increase in the mean temperature was observed. Observations suggest low wind intensities during the period.

Data presented in this study include aerosol size distribution, CCN spectra, BC concentration and non-refractory chemical composition, measured from 16 to 31 March 2012. All measurements are reported at local ambient pressure and temperature conditions. Local time (UTC minus 3 h) is used throughout this study. In the following a description of the instrumentation used is provided.

2.2 Instrumentation

2.2.1 Cloud condensation nuclei counter (CCNC)

A single-column continuous-flow stream-wise thermal gradient CCN chamber (DMT CCNC-100, Roberts and Nenes, 2005; Lance et al., 2006) was used to measure the total polydisperse CCN number concentration as a function of time and supersaturation (SS). The effective water vapour supersaturation (S) was regulated by the temperature gradient applied between the upper and lower wetted end of the CCNC flow column, where the activation takes place. The particles having lower SS_{crit} than the SS in the

column are activated and grow into the supermicron size-range. Particles leaving the column are sized by an optical particle counter (OPC) and counted as CCNs if their diameter is larger than a threshold size of 0.75 μm .

The CCNC was operated at a total flow rate of 0.5 L min^{-1} with a sheath-to-aerosol flow ratio of 10. One measurement cycle included measurements at 5 different SS (0.20–1.0 %). The CCN concentration at each SS was measured for 5 min. Data reported here include only under supersaturation steady state. The factory calibration based on $(\text{NH}_4)_2\text{SO}_4$ was used.

2.2.2 Differential Mobility Particle Sizer (DMPS)/Condensation Particle Counter (CPC)

A Differential Mobility Particle Sizer (DMPS) was used to measure number-size distribution of aerosol particles with diameters in the range 10–500 nm. A condensation particle counters (CPC TSI 3010) was used for particle detection after the DMA. The CPC was calibrated for counting efficiency as a function of particle size. During the measurements, the DMA was operated in a stepwise scanning mode starting from 10 nm diameter and stepped upwards or downward respectively. 22 diameter steps were used in the scans for a total of 22 mobility channels. A single scan over the whole size range took 5 min. A CPC (TSI 3772) was operated in parallel for comparison with particle number concentrations from the DMPS. Based on such intercomparison, DMPS data has been corrected by a factor of 1.12. Intercomparison has been performed for particle numbers below 10 000 cm^{-3} due to decreased accuracy in the CPC. Undercounting of the DMPS may have been caused by slight deviations of the sample and sheath flow rates from the nominal values, or a DMA transfer probability lower than assumed.

2.2.3 A Multi-Angle Absorption Photometer (MAAP)

Real-time BC mass concentration was measured using the Multi-Angle Absorption Photometer (MAAP, Thermo Scientific model 5012). The instrument measures simulta-

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

activated fraction, i.e., the ratio of the CCN number concentration relative to the integrated DMPS number concentration. One interesting feature revealed by Fig. 2a is the low variability of CCN concentration activated at 0.2%. Even during the large aerosol concentration event on the 16 October 2012, CCN concentration does not exceed 2000 cm^{-3} , showing an enhancement factor as high as 2. Conversely, CCN concentration activated at 0.4% SS enhanced over four times during the same event. A summary of CCN concentration observed during the period is shown on Table 1. Overall the activated fraction varied by a factor of $\sim 4\text{--}6$, indicating that most of the high variability of CCN number concentration is due to the variations of the chemical composition, while a smaller part of it can be attributed to variability of the aerosol properties such as shape of the size distribution and the total particle number concentration. The mean hourly activated fraction is shown in Fig. 2c. The activated fraction strongly decreases in the morning hours, probably due to rush hour emission, consistent with observations of Lance et al. (2013). Overall the activated fraction are under 0.4, with mean values of 0.10 ± 0.05 for $\text{SS} = 0.2\%$ and 0.29 ± 0.15 for $\text{SS} = 1.0\%$. Throughout the day, the activated fraction increases, probably due to a combination of increase in average diameter as well as production of secondary organic and inorganic aerosols. Mean characteristics of the aerosol size distribution is shown in Fig. 3. The aerosol size distribution was most of the time monomodal, occasionally bimodal. Figure 3a depicts such a feature for the pollution event for 16 October 2012. In many occasions it is possible to see nucleation events occurring, as is observed at 07:00 and 09:00 LT, when a large number of small particles below 40 nm are observed, as a result of fresh traffic emission during morning hours. In the next few hours these particles seem to grow by condensation, the size distribution becomes more peaked and shift to the right. On the 19 October (Fig. 3b), the aerosol concentration was lower than those observed during 16 October, and the nucleation process is not evident. The temporal evolution of the mean aerosol concentration (CN) is also marked by the appearance of several peaks that alternates with low CN values (Fig. 3c). Given the strong coupling between atmospheric processes, including aerosol growth and formation of secondary aerosols,

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 $SS = 0.20\%$.

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-

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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,

and p_0 , the saturation vapour pressure of water, and can be written as

$$S = a_w \exp\left(\frac{4\sigma M_w}{RT\rho_w D_{\text{drop}}}\right) \quad (1)$$

where a_w is the water activity of the solution, ρ_w is the density of water, M_w is the molecular weight of water, σ_{sol} is the surface tension of the solution/air interface (considered constant on this study, 0.072 J m^{-2}), R is the universal gas constant, T is temperature, and D_{drop} is the diameter of the droplet.

Following Petters and Kreidenweis (2007), we used a semi-empirical water activity parameterization for definition of a_w

$$a_w = \left(1 + \kappa \frac{D_0^3}{D_{\text{Drop}}^3 - D_0^3}\right)^{-1} \quad (2)$$

where κ is the hygroscopicity parameter, and D_0 the dry particle diameter. Substituting a_w in Eq. (1) with Eq. (2) provides the κ -Köhler equation:

$$S = \left(1 + \kappa \frac{D_0^3}{D_{\text{Drop}}^3 - D_0^3}\right)^{-1} \exp\left(\frac{4\sigma M_w}{RT\rho_w D_{\text{drop}}}\right) \quad (3)$$

The SS_{crit} of a particle with properties (D_0, κ) corresponds to the maximum value of S obtained with Eq. (3) considering D_{drop} as the independent variable. The SS_{crit} of any dry diameter with known chemical composition can be determined by numerical iteration considering variation on D_{drop} and determining the equivalent equilibrium saturation rate.

The time resolved mass fractions defined above can be used to feed the equation for $\kappa = f_{\text{org}}K_{\text{org}} + f_{\text{inor}}K_{\text{inor}}$ (Dusek et al., 2010; Rose et al., 2011) to get the ACMS/MAAP

derived κ as a function of time, where we use $\kappa_{\text{org}} = 0.1$, and $\kappa_{\text{inor}} = 0.7$ (Dusek et al., 2010). Since the κ values of the different inorganic salts are similar, the overall κ value experience large variations. The mean ACSM/MAAP derived κ value for the period studied was 0.15 ± 0.04 (0.10 ± 0.03 for inorganic fraction). This value is lower than the global mean κ values for continental regions (0.27 ± 0.21) and much lower than those value for marine regions (0.72 ± 0.24) (Andreae and Rosenfeld, 2008; Pringle et al., 2010). This is probably a result of relatively low concentration of inorganics.

3.2.1 Internal mixture and ACSM chemical composition

In this section we evaluate the relation of simulated and measured N_{CCN} . We assume internal mixture of aerosol chemical composition derived from the ACSM, and uses the aerosol size distribution determined by the DMPS to determine the N_{CCN} at a certain supersaturation.

Initially, the κ size independent solubility value is determined using the values of Dusek et al. (2010) ($\kappa = 0.1$ for organics and $\kappa = 0.7$ for inorganics). In this case, the total modelled concentration for a certain supersaturation is determined as the sum of DMPS concentration for those classes of diameters whose critical supersaturation are lower or equals to the supersaturation under consideration. In the case of intermediate values of supersaturation, linear interpolation is used.

The modelled results indicate an overestimation of N_{CCN} , with increasing overestimation factor with critical supersaturation. The slope of the fitted line increases from 1.38 to 1.56 when going from 0.20 % to 1.0 % of supersaturation (Table 3a), shown on Fig. 5, while the correlation coefficients (R^2) tend to go from 0.39 to 0.81, showing that the data scattering tends to decrease as the supersaturation increases and the overestimation tends to be higher as the particle size decreases. The mean relation between N_{CCN} simulated and observed was 1.30 ± 0.45 for 0.20 % supersaturation and 1.57 ± 0.30 for 1.0 % supersaturation. A lower error at lower supersaturation can be expected due to the larger importance of particle size regarding particle chemical composition when one considers larger sizes, as expected. Overall, the impact of chemical

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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 sulphate 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

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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

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 $\pm 22\%$ considering a mean size-dependent soluble fraction based on MOUDI+PIXE

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



analysis. The knowledge of the soluble salt fraction is sufficient for description of CCN activity at São Paulo, which is consistent with other closure studies conducted in the past.

The results from these measurements can be used to constrain the uncertainty associated with assumptions in GCM modelling studies of the aerosol indirect effect. As suggested in recent study (Sotiropoulou et al., 2007) if the CCN prediction error is on the order of 20 % it may not contribute a significant source of error in the assessment of the aerosol indirect effect.

Acknowledgements. This research was funded from FAPESP (São Paulo Science Foundation).

References

Albuquerque, T. T., Andrade, M. F., and Ynoue, R. Y.: Characterization of atmospheric aerosols in the city of São Paulo, Brazil: comparisons between polluted and unpolluted periods, *Environ. Monit. Assess.*, 184, 969–984, doi:10.1007/s10661-011-2013-y, 2012.

Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnop, D. R.: A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, *J. Aerosol Sci.*, 35, 909–922, doi:10.1016/j.jaerosci.2004.02.007, 2004.

Andreae, M. O. and Rosenfeld, D.: Aerosol-cloud-precipitation interactions – Part 1: The nature and sources of cloud-active aerosols, *Earth Sci. Rev.*, 89, 13–41, 2008.

Bougiatioti, A., Fountoukis, C., Kalivitis, N., Pandis, S. N., Nenes, A., and Mihalopoulos, N.: Cloud condensation nuclei measurements in the marine boundary layer of the Eastern Mediterranean: CCN closure and droplet growth kinetics, *Atmos. Chem. Phys.*, 9, 7053–7066, doi:10.5194/acp-9-7053-2009, 2009.

Bougiatioti, A., Nenes, A., Fountoukis, C., Kalivitis, N., Pandis, S. N., and Mihalopoulos, N.: Size-resolved CCN distributions and activation kinetics of aged continental and marine aerosol, *Atmos. Chem. Phys.*, 11, 8791–8808, doi:10.5194/acp-11-8791-2011, 2011.

Broekhuizen, K., Chang, R.Y.-W., Leaitch, W. R., Li, S.-M., and Abbatt, J. P. D.: Closure between measured and modeled cloud condensation nuclei (CCN) using size-resolved aerosol

32371

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

compositions in downtown Toronto, *Atmos. Chem. Phys.*, 6, 2513–2524, doi:10.5194/acp-6-2513-2006, 2006.

Cantrell, W., Shaw, G., Cass, G. R., Chowdhury, Z., Hughes, L. S., Prather, K. A., Guazzotti, S. A., and Coffee, K. R.: Closure between aerosol particles and cloud condensation nuclei at Kaashidhoo Climate Observatory, *J. Geophys. Res.*, 106, 28711–28718, 2001.

Castanho, A. and Artaxo, P.: Wintertime and summertime São Paulo aerosol source apportionment study, *Atmos. Environ.*, 35, 4889–4902, 2001.

CETESB – Companhia de Tecnologia de Saneamento Ambiental: Relatório Anual de Qualidade do Ar no Estado de São Paulo 2006, São Paulo, 2007.

Chang, R. Y. W., Liu, P. S. K., Leaitch, W. R., and Abbatt, J. P. D.: Comparison between measured and predicted CCN concentrations at Egbert, Ontario: focus on the organic aerosol fraction at a semi-rural site, *Atmos. Environ.*, 41, 8172–8182, 2007.

Conant, W. C., VanReken, T. M., Rissman, T. A., Varutbangkul, V., Jonsson, H. H., Nenes, A., Jimenez, J. L., Delia, A. E., Bahreini, R., Roberts, G. C., Flagan, R. C., and Seinfeld, J. H.: Aerosol-cloud drop concentration closure in warm cumulus, *J. Geophys. Res.*, 109, D13204, doi:10.1029/2003JD004324, 2004.

Dusek, U., Frank, G. P., Curtius, J., Drewnick, F., Schneider, J., Kürten, A., Rose, D., Andreae, M. O., Borrmann, S., and Pöschl, U.: Enhanced organic mass fraction and decreased hygroscopicity of cloud condensation nuclei (CCN) during new particle formation events, *Geophys. Res. Lett.*, 37, L03804, doi:10.1029/2009GL040930, 2010.

Ervens, B., Cubison, M. J., Andrews, E., Feingold, G., Ogren, J. A., Jimenez, J. L., DeCarlo, P., and Nenes, A.: Prediction of cloud condensation nucleus number concentration using measurements of aerosol size distributions and composition and light scattering enhancement due to humidity, *J. Geophys. Res.*, 112, D10S32, doi:10.1029/2006JD007426, 2007.

Gasparini, R., Li, R., Collins, D. R., Ferrare, R. A., and Brackett, V. G.: Application of aerosol hygroscopicity measured at the Atmospheric Radiation Measurement Program's Southern Great Plains site to examine composition and evolution, *J. Geophys. Res.*, 111, D05S12, doi:10.1029/2004JD005448, 2006.

Gunthe, S. S., King, S. M., Rose, D., Chen, Q., Roldin, P., Farmer, D. K., Jimenez, J. L., Artaxo, P., Andreae, M. O., Martin, S. T., and Pöschl, U.: Cloud condensation nuclei in pristine tropical rainforest air of Amazonia: size-resolved measurements and modeling of atmospheric aerosol composition and CCN activity, *Atmos. Chem. Phys.*, 9, 7551–7575, doi:10.5194/acp-9-7551-2009, 2009.

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

- Gunthe, S. S., Rose, D., Su, H., Garland, R. M., Achtert, P., Nowak, A., Wiedensohler, A., Kuwata, M., Takegawa, N., Kondo, Y., Hu, M., Shao, M., Zhu, T., Andreae, M. O., and Pöschl, U.: Cloud condensation nuclei (CCN) from fresh and aged air pollution in the megacity region of Beijing, *Atmos. Chem. Phys.*, 11, 11023–11039, doi:10.5194/acp-11-11023-2011, 2011.
- 5 Gurjar, B., Butler, T., Lawrence, M., and Lelieveld, J.: Evaluation of emissions and air quality in megacities, *Atmos. Environ.*, 42, 1593–1606, doi:10.1016/j.atmosenv.2007.10.048, 2008.
- Hänel, G.: Radiation budget of the boundary layer – Part 2: Simultaneous measurement of mean solar volume absorption and extinction coefficients of particles, *Beitr. Phys. Atmos.*, 10
60, 241–247, 1987.
- Köhler, H.: The nucleus in and the growth of hygroscopic droplets, *T. Faraday Soc.*, 32, 1152–1161, 1936.
- Kuhn, U., Ganzeveld, L., Thielmann, A., Dindorf, T., Schebeske, G., Welling, M., Sciare, J., Roberts, G., Meixner, F. X., Kesselmeier, J., Lelieveld, J., Kolle, O., Ciccioli, P., Lloyd, J., Trentmann, J., Artaxo, P., and Andreae, M. O.: Impact of Manaus City on the Amazon Green
15 Ocean atmosphere: ozone production, precursor sensitivity and aerosol load, *Atmos. Chem. Phys.*, 10, 9251–9282, doi:10.5194/acp-10-9251-2010, 2010.
- Kuwata, M., Kondo, Y., Mochida, M., Takegawa, N., and Kawamura, K.: Dependence of CCN activity of less volatile particles on the amount of coating observed in Tokyo, *J. Geophys. Res.*, 20
112, D11207, doi:10.1029/2006JD007758, 2007.
- Kuwata, M., Kondo, Y., Miyazaki, Y., Komazaki, Y., Kim, J. H., Yum, S. S., Tanimoto, H., and Matsueda, H.: Cloud condensation nuclei activity at Jeju Island, Korea in spring 2005, *Atmos. Chem. Phys.*, 8, 2933–2948, doi:10.5194/acp-8-2933-2008, 2008.
- Kuwata, M., Kondo, Y., and Takegawa, N.: Critical condensed mass for activation of
25 black carbon as cloud condensation nuclei in Tokyo, *J. Geophys. Res.*, 114, D20202, doi:10.1029/2009JD012086, 2009.
- Lance, S., Raatikainen, T., Onasch, T. B., Worsnop, D. R., Yu, X.-Y., Alexander, M. L., Stolzenburg, M. R., McMurry, P. H., Smith, J. N., and Nenes, A.: Aerosol mixing state, hygroscopic growth and cloud activation efficiency during MIRAGE 2006, *Atmos. Chem. Phys.*, 13, 5049–5062, doi:10.5194/acp-13-5049-2013, 2013.
- Liu, P. S. K., Leaitch, W. R., Banic, C. M., Li, S.-M., Ngo, D., and Megaw, W. J.: Aerosol observations at Chebogue Point during the 1993 North Atlantic Regional Experiment: relationships

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

among cloud condensation nuclei, size distribution, and chemistry, *J. Geophys. Res.*, 101, 28971–28990, 1996.

Matsumoto, K., Tanaka, H., Nagao, I., and Ishizaka, Y.: Contribution of particulate sulfate and organic carbon to cloud condensation nuclei in the marine atmosphere, *Geophys. Res. Lett.*, 24, 655–658, 1997.

McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M. C., Feingold, G., Fuzzi, S., Gysel, M., Laaksonen, A., Lohmann, U., Mentel, T. F., Murphy, D. M., O'Dowd, C. D., Snider, J. R., and Weingartner, E.: The effect of physical and chemical aerosol properties on warm cloud droplet activation, *Atmos. Chem. Phys.*, 6, 2593–2649, doi:10.5194/acp-6-2593-2006, 2006.

Mei, F., Setyan, A., Zhang, Q., and Wang, J.: CCN activity of organic aerosols observed downwind of urban emissions during CARES, *Atmos. Chem. Phys. Discuss.*, 13, 9355–9399, doi:10.5194/acpd-13-9355-2013, 2013.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of composition dependent collection efficiencies for the aerodyne aerosol mass spectrometer using field data, *Aerosol Sci. Tech.*, 46, 258–271, 2012.

Müller, T., Henzing, J. S., de Leeuw, G., Wiedensohler, A., Alastuey, A., Angelov, H., Bizjak, M., Collaud Coen, M., Engström, J. E., Gruening, C., Hillamo, R., Hoffer, A., Imre, K., Ivanow, P., Jennings, G., Sun, J. Y., Kalivitis, N., Karlsson, H., Komppula, M., Laj, P., Li, S.-M., Lunder, C., Marinoni, A., Martins dos Santos, S., Moerman, M., Nowak, A., Ogren, J. A., Petzold, A., Pichon, J. M., Rodriguez, S., Sharma, S., Sheridan, P. J., Teinilä, K., Tuch, T., Viana, M., Virkkula, A., Weingartner, E., Wilhelm, R., and Wang, Y. Q.: Characterization and intercomparison of aerosol absorption photometers: result of two intercomparison workshops, *Atmos. Meas. Tech.*, 4, 245–268, doi:10.5194/amt-4-245-2011, 2011.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol, *Aerosol Sci. Tech.*, 45, 780–794. doi:10.1080/02786826.2011.560211, 2011.

Padró, L. T., Moore, R. H., Zhang, X., Rastogi, N., Weber, R. J., and Nenes, A.: Mixing state and compositional effects on CCN activity and droplet growth kinetics of size-resolved CCN in an urban environment, *Atmos. Chem. Phys.*, 12, 10239–10255, doi:10.5194/acp-12-10239-2012, 2012.

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.*, 7, 1961–1971, doi:10.5194/acp-7-1961-2007, 2007.
- Petzold, A. and Schönlinner, M.: Multi-angle absorption photometry – a new method for the measurement of aerosol light absorption and atmospheric black carbon, *J. Aerosol Sci.*, 35, 421–441, 2004.
- Petzold, A., Schloesser, M., Sheridan, P. J., Arnott, W. P., Ogren, J. A., and Virkkula, A.: Evaluation of multi-angle absorption photometry for measuring aerosol light absorption, *Aerosol Sci. Tech.*, 39, 40–51, 2005.
- Pringle, K. J., Tost, H., Pozzer, A., Pöschl, U., and Lelieveld, J.: Global distribution of the effective aerosol hygroscopicity parameter for CCN activation, *Atmos. Chem. Phys.*, 10, 5241–5255, doi:10.5194/acp-10-5241-2010, 2010.
- Quinn, P. K., Bates, T. S., Coffman, D., Onasch, T. B., Worsnop, D., Baynard, T., de Gouw, J. A., Goldan P. D., Kuster, W. C., Williams, E., Roberts, J. M., Lerner B., Stohl A., Petersson, A., and Lovejoy, E. R.: Impacts of sources and aging on submicrometer aerosol properties in the marine boundary layer across the Gulf of Maine, *J. Geophys. Res.*, 111, D23S36, doi:10.1029/2006JD007582, 2006.
- Rissler, J., Swietlicki, E., Zhou, J., Roberts, G., Andreae, M. O., Gatti, L. V., and Artaxo, P.: Physical properties of the sub-micrometer aerosol over the Amazon rain forest during the wet-to-dry season transition – comparison of modeled and measured CCN concentrations, *Atmos. Chem. Phys.*, 4, 2119–2143, doi:10.5194/acp-4-2119-2004, 2004.
- Roberts, G. C., Artaxo, P., Zhou, J., Sweitlicki, E., and Andreae, M. O.: Sensitivity of CCN spectra on chemical and physical properties of aerosol: a case study from the Amazon Basin, *J. Geophys. Res.*, 107, 8070, doi:10.1029/2001JD000583, 2002.
- Rose, D., Gunthe, S. S., Su, H., Garland, R. M., Yang, H., Berghof, M., Cheng, Y. F., Wehner, B., Achtert, P., Nowak, A., Wiedensohler, A., Takegawa, N., Kondo, Y., Hu, M., Zhang, Y., Andreae, M. O., and Pöschl, U.: Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China – Part 2: Size-resolved aerosol chemical composition, diurnal cycles, and externally mixed weakly CCN-active soot particles, *Atmos. Chem. Phys.*, 11, 2817–2836, doi:10.5194/acp-11-2817-2011, 2011.
- Sánchez-Ccoyollo, O. R. and Andrade, M. F.: The influence of meteorological conditions on the behavior of pollutants concentrations in São Paulo, Brazil, *Environ. Pollut.*, 116, 257–263, 2002.

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Shinozuka, Y., Clarke, A. D., DeCarlo, P. F., Jimenez, J. L., Dunlea, E. J., Roberts, G. C., Tomlinson, J. M., Collins, D. R., Howell, S. G., Kapustin, V. N., McNaughton, C. S., and Zhou, J.: Aerosol optical properties relevant to regional remote sensing of CCN activity and links to their organic mass fraction: airborne observations over Central Mexico and the US West Coast during MILAGRO/INTEX-B, *Atmos. Chem. Phys.*, 9, 6727–6742, doi:10.5194/acp-9-6727-2009, 2009.

Sotiropoulou, R. E. P., Nenes, A., Adams, P. J., and Seinfeld, J. H.: Cloud condensation nuclei prediction error from application of Köhler theory: importance for the aerosol indirect effect, *J. Geophys. Res.*, 112, D12202, doi:10.1029/2006JD007834, 2007.

Van Ranken, T. M., Rissman, T. A., Roberts, G. C., Varutbangukul, V., Jonsson, H., Flagan, R., and Seinfeld, J. H.: Toward aerosol/cloud condensation nuclei (CCN) closure during CRYSTAL-FACE, *J. Geophys. Res.*, 108, 4633, doi:10.1029/2003JD003582, 2003.

Vasconcellos, P. C., Souza, D. Z., Simone, G. A., Araújo, M. P., Naoto, E., Nascimento, K. H., Cavalcante, F. S., Santos, M., Smichowski, P., and Behrentz, E.: Comparative study of the atmospheric chemical composition of three South American cities, *Atmos. Environ.*, 45, 5770–5777, 2011.

Wang, J., Lee, Y.-N., Daum, P. H., Jayne, J., and Alexander, M. L.: Effects of aerosol organics on cloud condensation nucleus (CCN) concentration and first indirect aerosol effect, *Atmos. Chem. Phys.*, 8, 6325–6339, doi:10.5194/acp-8-6325-2008, 2008.

Wiedensohler, A., Cheng, Y. F., Nowak, A., Wehner, B., Achtert, P., Berghof, M., Birmili, W., Wu, Z. J., Hu, M., Zhu, T., Takegawa, N., Kita, K., Kondo, Y., Lou, S. R., Hofzumahaus, A., Holland, F., Wahner, A., Gunthe, S. S., Rose, D., Su, H., and Pöschl, U.: Rapid aerosol particle growth and increase of cloud condensation nucleus activity by secondary aerosol formation and condensation: a case study for regional air pollution in northeastern China, *J. Geophys. Res.*, 114, D00G08, doi:10.1029/2008JD010884, 2009.

Ynoue, R. Y. and Andrade, M. F. Size-resolved mass balance of aerosol particles over the São Paulo Metropolitan area of Brazil, *Aerosol Sci. Tech.*, 38, 52–62, doi:10.1080/02786820490466756, 2004

Yum, S. S., Hudson, J. G., Song, K. Y., and Choi, B.-C.: Springtime cloud condensation nuclei concentrations on the west coast of Korea, *Geophys. Res. Lett.*, 32, L09814, doi:10.1029/2005GL022641, 2005.

Yum, S. S., Roberts, G., Kim, J. H., Song, K. Y., and Kim, D. Y.: Submicron aerosol size distributions and cloud condensation nuclei concentrations measured at Gosan, Korea, during the

Atmospheric brown clouds East Asian Regional Experiment 2005, J. Geophys. Res., 112, D22S32, doi:10.1029/2006JD008212, 2007.

Zhang, Q., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J.-L.: Time- and size-resolved chemical composition of submicron particles in Pittsburgh: implications for aerosol sources and processes, J. Geophys. Res., 110, D07S09, doi:10.1029/2004JD004649, 2005.

5

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Details on the mean measured N_{CCN} values furnished by CCNC for São Paulo from 16 to 31 October 2012.

Supersaturation	0.2 %	0.4 %	0.6 %	0.8 %	1.0 %
Mean N_{CCN}	1090 ± 328	2202 ± 1035	2776 ± 1331	3175 ± 1503	3570 ± 1695
Activated fraction	0.10 ± 0.05	0.19 ± 0.09	0.23 ± 0.10	0.26 ± 0.11	0.28 ± 0.12

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

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

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

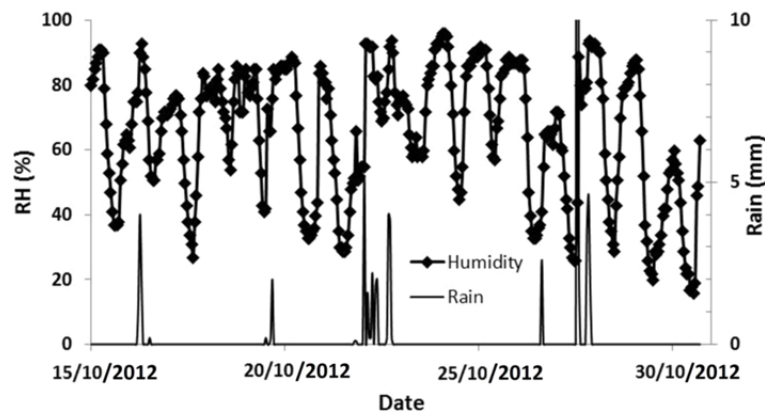
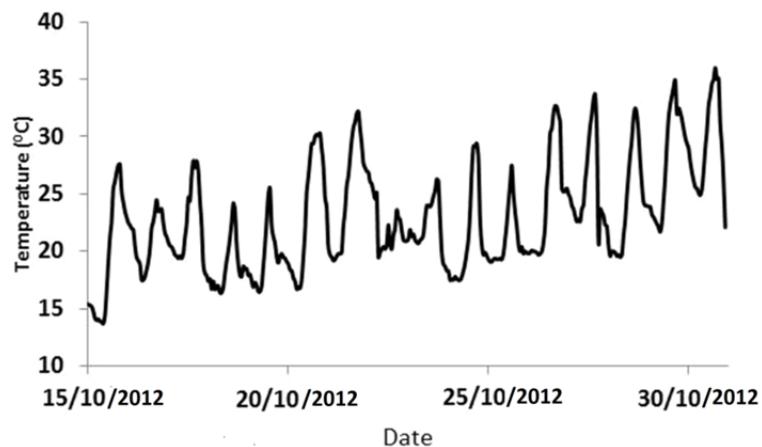


Fig. 1. Diurnal variation of the (a) temperature and (b) RH at the sampling site during the studied period.

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

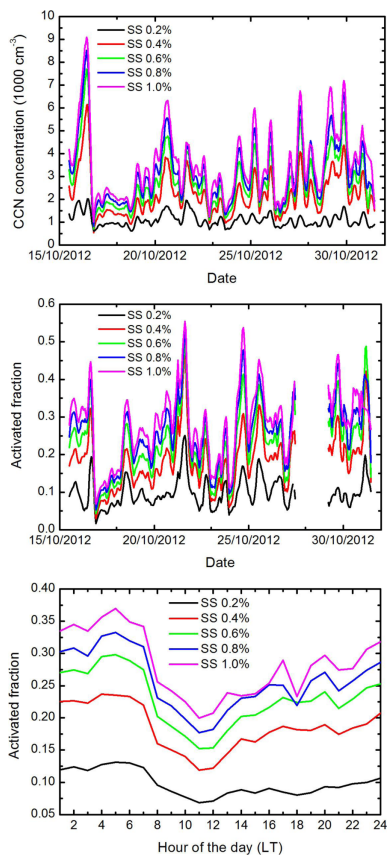


Fig. 2. Time series of **(a)** CCN number concentration, **(b)** the activated fraction ($\#CCN/N_{10-500}$) and **(c)** the mean hourly averaged over the whole period. The different colours represent the different supersaturations (SS).

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

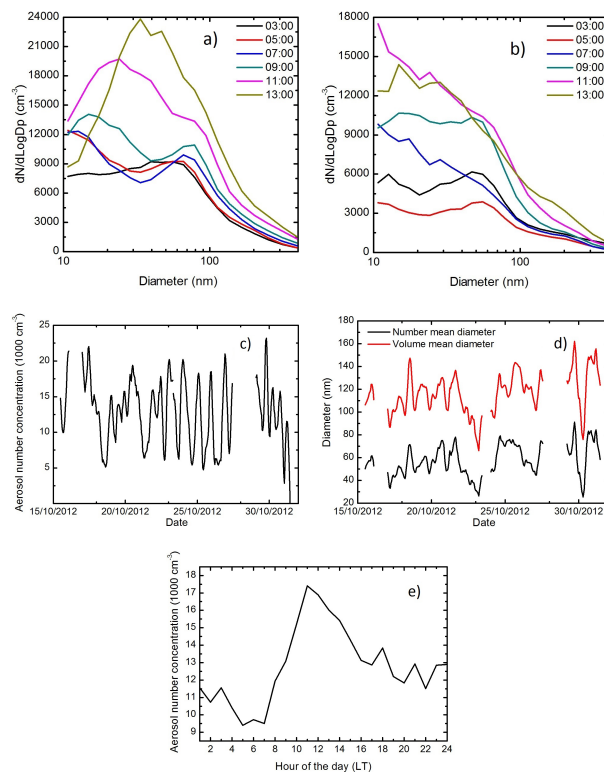


Fig. 3. (a) aerosol size distribution during 16 October 2012 in SP (b) the same as in (a), but for 17 October (c) Total aerosols concentration from 10 nm to 500 nm (d) mean aerosol diameter and mean aerosol volumetric diameter, and (e) Mean hourly aerosol total concentration.

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

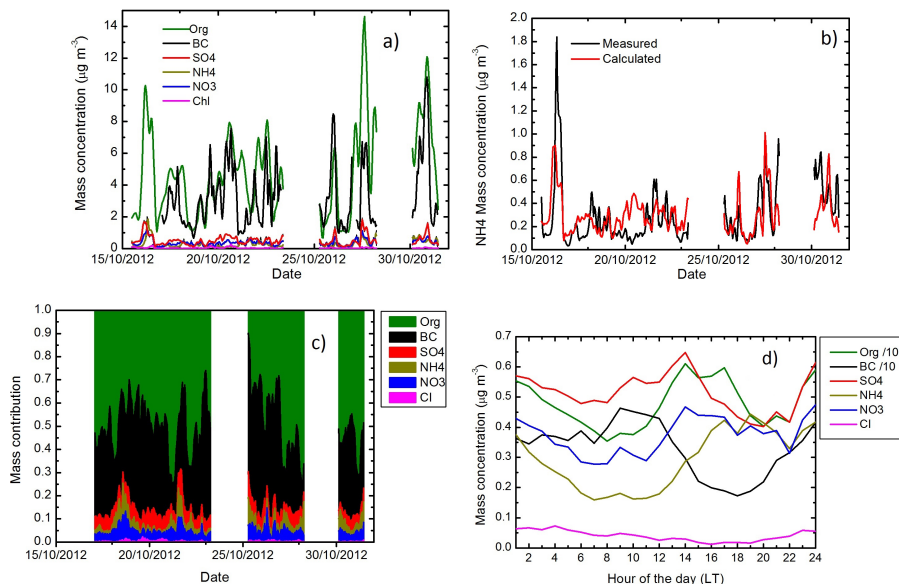


Fig. 4. Chemical composition of the aerosol, measured by the ACMS and the MAAp. **(a)** mass concentration of the individual species, **(b)** mass concentration of the measured NH_4 and the calculated amount needed for complete neutralization, **(c)** the mass fractions of the organics, NH_4 , NO_3 ,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

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

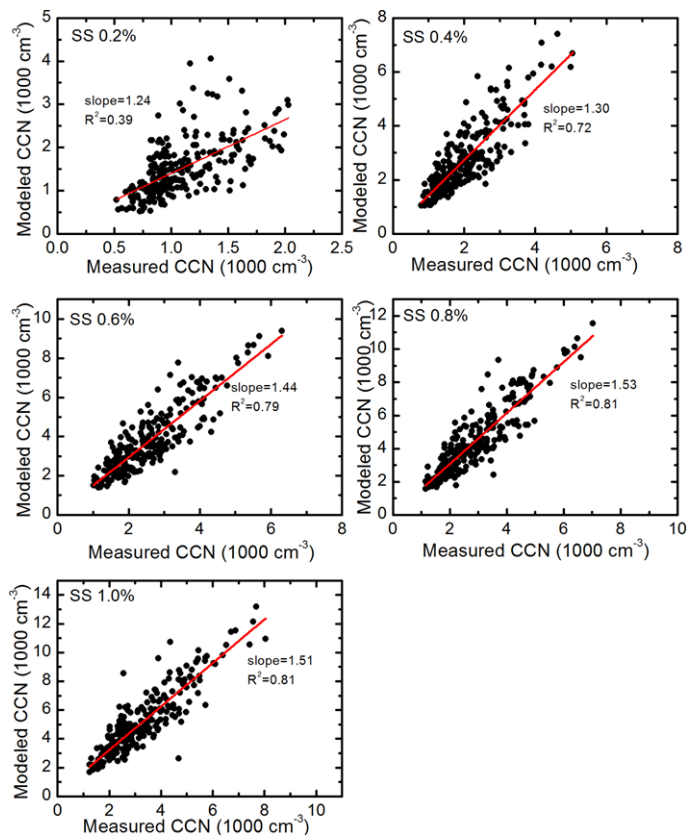


Fig. 5. Comparison of modelled and measured CCN concentrations using internal mixing for the 5 measured supersaturation (0.2%, 0.4%, 0.6%, 0.8%, and 1.0% SS).

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

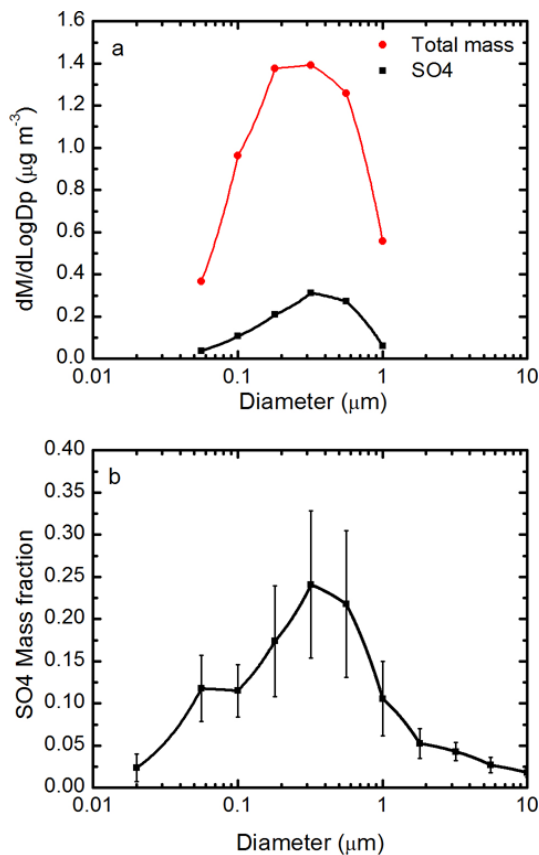


Fig. 6. Mean value of **(a)** $dM/d\log d$ ($\mu\text{g m}^{-3}$) for the period of 15 August to 5 September 2012 and **(b)** SO₄ mass fraction for the same period.

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

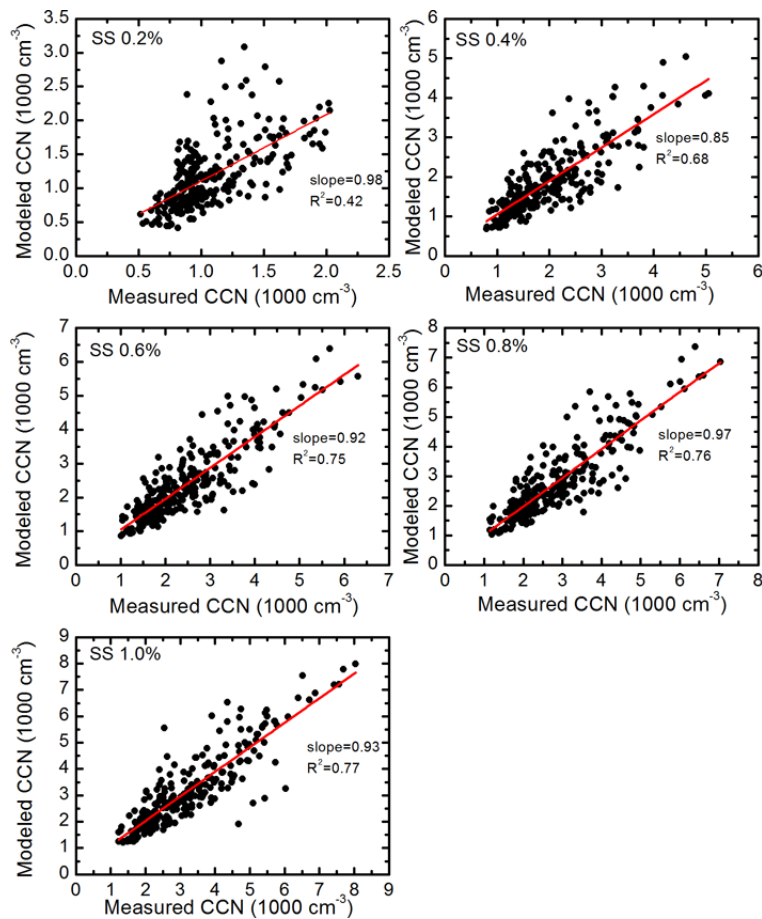


Fig. 7. Same as Fig. 5, but using the size dependence based on MOUDI+PIXE analysis.

Measured and modelled Cloud Condensation Nuclei (CCN) concentration

G. P. Almeida et al.

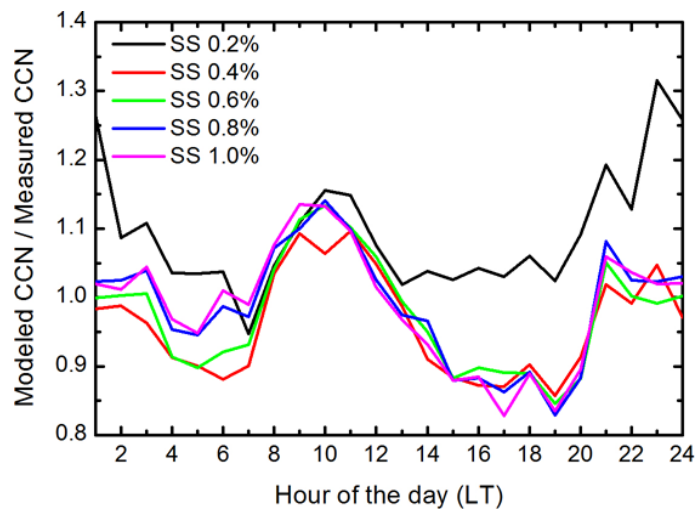


Fig. 8. Mean value of modelled N_{CCN} /Observed N_{CCN} as a function of local time.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)