Size-resolved cloud condensation nuclei (CCN) activity and closure analysis at the HKUST Supersite in Hong Kong

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Abstract

The cloud condensation nuclei (CCN) properties of atmospheric aerosols were measured on May 1-30, 2011 at a coastal site in Hong Kong. Size-resolved CCN activation curves, the ratio of number concentration of CCN ($N_{CCN}$) to aerosol concentration ($N_{CN}$) as a function of particle size, were obtained at supersaturation ($SS$) = 0.15%, 0.35%, 0.50%, and 0.70% using a DMT CCN counter (CCNc) and a TSI scanning mobility particle sizer (SMPS). The mean bulk size-integrated $N_{CCN}$ ranged from ~500 cm$^{-3}$ at $SS = 0.15\%$ to ~2100 cm$^{-3}$ at $SS = 0.70\%$, and the mean bulk $N_{CCN}/N_{CN}$ ratio ranged from 0.16 at $SS = 0.15\%$ to 0.65 at $SS = 0.70\%$. The average critical mobility diameters ($D_{50}$) at $SS = 0.15\%, 0.35\%, 0.50\%, \text{and} 0.70\%$ were 116 nm, 67 nm, 56 nm, and 46 nm, respectively. The corresponding average hygroscopic parameters ($\kappa_{CCN}$) were 0.39, 0.36, 0.31, and 0.28. The decrease in $\kappa_{CCN}$ can be attributed to the increase in organic to inorganic volume ratio as particle size decreases, as measured by an Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). The $\kappa_{CCN}$ correlates reasonably well with $\kappa_{AMS,SR}$ based on size-resolved AMS measurements: $\kappa_{AMS,SR} = \kappa_{org} \times f_{org} + \kappa_{inorg} \times f_{inorg}$, where $f_{org}$ and $f_{inorg}$ are the organic and inorganic volume fractions, respectively, $\kappa_{org} = 0.1$ and $\kappa_{inorg} = 0.6$, with a $R^2$ of 0.51.

In closure analysis, $N_{CCN}$ was estimated by integrating the measured size-resolved $N_{CN}$ for particles larger than $D_{50}$ derived from $\kappa$ assuming internal mixing state. Estimates using $\kappa_{AMS,SR}$ show that the measured and predicted $N_{CCN}$ were generally within 10% of each other at all four SS. The deviation increased to 26% when $\kappa_{AMS}$ was calculated from bulk PM1 AMS measurements of particles because PM1 was dominated by particles of ~200 nm to 500 nm in diameter, which had a larger inorganic fraction than those of $D_{50}$ (particle diameter < 200 nm). A constant $\kappa = 0.33$ (the average value of $\kappa_{AMS,SR}$ over the course of campaign) was found to give an $N_{CCN}$ prediction within 12% of the actual measured values. We also compared $N_{CCN}$ estimates based on the measured average $D_{50}$ and the average size-resolved CCN activation ratio to examine the relative importance of hygroscopicity and mixing state. $N_{CCN}$ was found to be relatively more sensitive to the mixing state and hygroscopicity at a high $SS = 0.70\%$ and a low $SS = 0.15\%$, respectively.
1 Introduction

Atmospheric aerosols can act as cloud condensation nuclei (CCN) and affect cloud formation by influencing the CCN number concentration ($N_{CCN}$) and the size of cloud droplets. Whether aerosol particles will eventually form cloud droplets under a set atmospheric condition mainly depends on their size, chemical composition, and mixing states. Predicting $N_{CCN}$ usually involves measuring the aerosol size distribution and making assumptions about the chemical composition associated to mixing state. Bulk chemical compositions and an assumption of internal mixing state (i.e., particles are identical mixtures of all participating species) are often used in predicting $N_{CCN}$ (Moore et al., 2012a; Wang et al., 2010). Ambient aerosols are complex mixtures and the aerosol compositions vary substantially with particle size. The hygroscopicity parameter ($\kappa$) is used to represent the effect of chemical composition on CCN activity (Petters and Kreidenweis, 2007, 2013). Size-resolved chemical compositions give a size-dependent $\kappa$ which leads to better $N_{CCN}$ predictions than those based on bulk compositions (Medina et al., 2007; Stroud et al., 2007; Wang et al., 2010).

While the real-time aerosol size-resolved chemical compositions such as non-refractory (NR)-species and black carbon (BC) can be obtained with an aerosol mass spectrometer and a single particle soot photometer, respectively, information on the mixing state is usually not available or incomplete. Various assumptions have been applied to describe the aerosol mixing state (Asa-Awuku et al., 2011; Bougiatioti et al., 2009; Cubison et al., 2008; Ervens et al., 2010; Lance et al., 2009; Lathem et al., 2013; Moore et al., 2012a; Rose et al., 2011; Wang et al., 2010). $N_{CCN}$ predictions assuming internal mixing are usually larger than measured values by 20% or even more, since this assumption overestimates the contribution of organics to $N_{CCN}$ (Rose et al., 2011; Wang et al., 2010; Wex et al., 2010). Another extreme assumption is external mixing, which is when the aerosol contains different types of particles but each particle consists of a single species (Textor et al., 2006; Zhang et al., 2010). Under this assumption, the number concentration ($N_{CN}$) of each type of particles is determined as the product of the total $N_{CN}$ and the volume fraction of the species. The $D_{50}$ of a species is calculated based on its $\kappa$ (Moore et al., 2012a; Wang et al., 2010) and $N_{CCN}$ is obtained by integrating $N_{CN}$ above $D_{50}$. Finally, the total $N_{CCN}$ is calculated by adding up all the predicted $N_{CCN}$ of the species. This simplified external
mixing state assumption could underestimate $N_{CCN}$. For example, Wang et al. (2010) reported an underestimation of ~20% in $N_{CCN}$ at supersaturation (SS) from 0.11% to 0.35%. Aerosol mixing state and chemical composition are thus important factors that need to be considered in the CCN prediction, especially in places where anthropogenic aerosol emission is strong and pollution is heavy (Ervens et al., 2010; Kammermann et al., 2010; Kerminen et al., 2012; Rose et al., 2010; Wang et al., 2010).

Recently, measurements of the condensation nuclei (CN) and CCN spectra simultaneously by combining a scanning mobility particle sizer (SMPS) and a CCN counter (CCNc) have been made (Asa-Awuku et al., 2010; Lance et al., 2009; Moore et al., 2012a; Moore et al., 2010; Padró et al., 2010; Rose et al., 2010). The size-resolved CCN activation ratios, i.e., the fraction of the measured $N_{CCN}/N_{CN}$ as a function of particle size, are the combined results of the size distribution, size resolved chemical composition, and the mixing state of the aerosols. Deng et al. (2013) estimated $N_{CCN}$ by integrating the product of the measured size-distributed $N_{CN}$ and the averaged size-resolved CCN activation ratio at each particle size bin measured at Wuqing in the North China Plain. The estimated and measured values differed by less than 6% at $SS = 0.06\%$ to 0.81%.

In recent years, the rapid urbanization and industrial development in the Pearl River Delta (PRD) have resulted in heavy air pollution, especially particulate matter (PM) pollution (Chan and Yao, 2008). Hong Kong, a typical coastal city south-east of the PRD, is affected by PM due to both local anthropogenic emissions and transportation of pollutants from the PRD (Lee et al., 2013).

In this study, we report for the first time size-resolved measurements of CCN activity in Hong Kong. We correlated the CCN-derived hygroscopicity ($\kappa_{CCN}$) with those estimated from the size-dependent aerosol chemical compositions determined by an Aerodyne high-resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, hereafter as AMS). Assuming internal mixtures, we carried out closure studies on $N_{CCN}$ prediction based on the size-distributions of $N_{CN}$ measured by a TSI SMPS and on the hygroscopicity values derived from size resolved and size integrated chemical compositions measured by AMS using Köhler theory,
Finally, using the average $D_{50}$ and the size-resolved CCN activation ratios from the CCN measurements, we examined the relative importance of hygroscopicity and mixing state in $N_{CCN}$ predictions at different $SS$.

2 Experimental methods

2.1 Sampling site and meteorological conditions

Measurements of aerosol chemical properties and CCN activity were carried out throughout the entire month of May 2011 at the Air Quality Research Supersite situated on the campus of the Hong Kong University of Science and Technology (HKUST) on the east coast of Hong Kong (see http://www.envr.ust.hk/research/research-facility/background-materials.html). High relative humidity ($RH$) with a mean of 81% and an average temperature of 26.0°C prevailed in this study. More information on the sampling location and meteorological conditions is available from Lee et al. (2013) and Li et al. (2013).

2.2 Instrument setup

2.2.1 Sample Inlet System

Ambient air was sampled at a flow rate of 16.67 L/min after passing through a PM2.5 cyclone on the roof of the Supersite (appropriately 20 m above sea level) and into a stainless steel sampling port supplying the on-line instruments of the TSI SMPS, the Droplet Measurement Technologies (DMT) dual column continuous-flow CCN counter (CCNc-200) and the Aerodyne AMS. The sampled air passed through a 1-m long diffusion drier (BMI, San Francisco, CA) filled with silica gel, thus its $RH$ was below 30% before it went into the above instruments for measurements.

2.2.2 CCN measurements
Size-resolved CCN spectra and activation ratios were measured with the CCNc-200 (Lance et al., 2006; Roberts and Nenes, 2005) coupled with a TSI SMPS, consisting of a differential mobility analyzer (DMA, TSI 3081L) and a water-based condensation particle counter (WCPC, TSI 3785).

As shown in Fig.1, charge-neutralized aerosols passed through the DMA for classification. The classified aerosols were then split into two streams: with one going into the WCPC for \(N_{\text{CN}}\) measurements and the other into the CCNc-200 for \(N_{\text{CCN}}\) measurements. The particle size distribution was measured every 6 min, with an up-scan time of 300 s. The sample flow rate was 1 L/min for the DMA, 0.5 L/min for the WCPC and the CCNc-200 each, and the closed-loop sheath air flow rate was 10 L/min. These flow rate settings allow SMPS (DMA+WCPC) measurements for particles ranging from 7 nm to 300 nm in mobility diameter \((D_m)\), which as we will show later, cover the \(D_{50}\) \((D_m)\) range of the particles studied. The sheath flow rate was continuously corrected using a mass flow controller. All flow rates were regularly checked and sizing accuracy for the SMPS and the CCNc-200 was verified with Polystyrene latex (PSL) spheres.

The CCNc-200 was operated at a total flow rate of 1 L/min, of which 0.5 L/min was for column A connected to the DMA to measure the size-resolved CCN spectrum and another 0.5 L/min was for column B connected to the sample inlet system to measure the total \(N_{\text{CCN}}\). A sheath-to-aerosol flow ratio of 10 was used. Latham and Nenes (2011) pointed out that the direct measurements could lead to underestimations of bulk \(N_{\text{CCN}}\) due to the depletion of water inside the column by a large amount of aerosols and recommended the use of size-resolved CCN measurement. In our measurements, the bulk \(N_{\text{CCN}}\) integrated from size-resolved CCN measurement using column A are usually fewer than 5000 cm\(^{-3}\) and they correlate well with that from the direct measurement using column B with a slope of 0.97 and correlation coefficient \((R^2)\) of 0.53 as shown in Fig.S1. We use bulk \(N_{\text{CCN}}\) calculated from column A for the comparison with \(N_{\text{CN}}\) from SMPS and for the closure study below. For every measurement cycle, four \(SS\) (0.15%, 0.35%, 0.50%, and 0.70%) were selected. Measurements at \(SS = 0.15\%) lasted 22 min whereas those at other \(SS\) lasted 12 min each for repeatability. CCNc temperature
transients during SS changes are known to produce unreliable spectra if they occur during a voltage up-scan (Moore et al., 2010). In our measurements, the instrument profiles were allowed up to ~2 min to stabilize whenever the temperature gradient was changed. At SS = 0.15%, a longer time (~4 min) was required for the stabilization of temperatures. Only data collected under stabilized temperatures were used for analysis.

The CCNc-200 was calibrated with size selected DMA ammonium sulfate particles at the four SS (Deng et al., 2011; Rose et al., 2008) regularly during the campaign. The instrument SS was derived from Köhler theory using a constant van’t Hoff factor of 2.5 for ammonium sulfate (Low, 1969; Tang and Munkelwitz, 1994; Young and Warren, 1992).

2.2.3 Aerosol chemical compositions

Non-refractory PM$_1$ (NR-PM$_1$) constituents of sulfate, nitrate, ammonium, chloride, and organics were measured with the AMS operated under V, pToF, and W modes. The principle behind the instrument has been described in detail elsewhere (DeCarlo et al., 2006) and will only be briefly described here. In pToF mode, the instrument performs particle sizing based on particle time-of-flight with the aid of a chopper and gives size-resolved chemical composition data in vacuum aerodynamic diameter ($D_{va}$) (DeCarlo et al., 2004). In V mode, the shorter traveling path for ions in the ion time-of-flight (ToF) chamber gives a mass spectral resolving power of approximately 2000 (DeCarlo et al., 2006) and better sensitivity. In W mode, the mass spectral resolving power is approximately 4000 (DeCarlo et al., 2006) but the signal-to-noise ratio is lower. The instrument was operated alternately between the V+pToF combined mode and the W mode for 5 min each. Evaluation of the ionization efficiency (IE) was carried out with ammonium nitrate particles weekly and both the flow rate and particle sizing were calibrated before and after the campaign. A more detailed description of the performance of the AMS during the campaign is presented by Li et al. (2013) and Lee et al. (2013). The AMS only measures NR-species but not elemental carbon (EC), sea salt, or crustal species. However, EC only accounts for less than 5% of the PM1 mass and hence can be neglected (Huang et al., 2014;
Lee et al., 2013). Sea salt and crustal species typically exist in the coarse mode and make negligible contributions to PM1.

2.3 Data analysis

2.3.1 CN and CCN data

The time series of $N_{\text{CN}}$ and $N_{\text{CCN}}$ distributions were obtained using the TSI Aerosol Instrument Manager (AIM) software (Wang and Flagan, 1989) and CCN acquisition software, respectively. The data collected during the voltage up-scan were employed for the inversion. The Scanning Mobility CCN Analysis (SMCA) was employed for calculating the size-resolved CCN activation fractions (Moore et al., 2010). The ratio of $N_{\text{CCN}}$ to $N_{\text{CN}}$ gives the size-resolved CCN activation fraction at each size. Then, the size-resolved CCN activation ratio was obtained by fitting the activation fraction with the sigmoidal function described by Equation 1 (see section 2.3.3) (Moore et al., 2010; Padró et al., 2010).

2.3.2 HR-ToF-AMS data

The standard toolkit of SQUIRREL (Sueper, 2011) was used for AMS data analysis. The collection efficiency ($CE$) used for this work was 0.5 and the relative ionization efficiency ($RIE$) of 1.2 for sulfate, 1.1 for nitrate, 1.3 for chloride, 1.4 for organics and 4.0 for ammonium were used as described by Li et al. (2013) and Lee et al. (2013). The size-resolved mass spectra for vacuum aerodynamic diameter ($D_{\text{va}}$) ranging from 50 nm to 2000 nm (DeCarlo et al., 2004) were obtained every 5 min on average. The mass concentration of each size bin was obtained by averaging with the two adjacent size bins to reduce the influence of noise (Rose et al., 2011). In order to relate the size-resolved AMS data with those of SMPS and CCNc measurements directly, the AMS $D_{\text{va}}$ size was divided by a factor of 1.7 to obtain the corresponding mobility equivalent diameter ($D_{m}$) (Cheng et al., 2006; DeCarlo et al., 2004; Lee et al., 2013). The volume fractions of size-resolved and bulk chemical compositions were calculated from the mass concentrations.
using densities of organics and inorganics of 1.3 g cm\(^{-3}\) and 1.75 g cm\(^{-3}\), respectively (Alfarra et al., 2006; Cross et al., 2007; Gunthe et al., 2009; King et al., 2007; Lee et al., 2013).

2.3.3 \(D_{50}\), \(\kappa_{CCN}\) and \(\kappa_{AMS}\)

The critical diameter \(D_{50}\), also known as the activation diameter, is the diameter at which 50% of the particles are activated at a specific SS. The \(D_{50}\) of a simple sigmoidal shaped activation ratio curve is determined by fitting the size-resolved activation fractions with the equation below:

\[
\frac{N_{CCN}}{N_{CN}} = \frac{B}{1 + \left(\frac{D_p}{D_{50}}\right)^c}
\]

where \(D_p\) is the dry mobility diameter, \(B\), \(c\), and \(D_{50}\) are fitting coefficients that describe the asymptote/plateau, the slope, and the inflection point of the sigmoid, respectively (Moore et al., 2010; Padró et al., 2012). The values of B were more than 90% during the whole campaign, indicating most of the particles were in the internal mixing state (Mei et al., 2013).

The measured hygroscopic parameter (\(\kappa_{CCN}\)) is determined from \(D_{50}\) by:

\[
\kappa_{CCN} = \frac{4A^2\sigma_{s/a}(T)}{27T^3D_{50}^2\ln^2S_c}
\]

where \(A = 8.69251\times10^{-6}\) Km\(^3\)J\(^{-1}\), \(\sigma_{s/a}(T)\) is the temperature-dependent surface tension of the solution/air interface, \(T\) is temperature and \(S_c\) is the critical saturation ratio. Pure water surface tension is assumed in the calculations of \(\kappa_{CCN}\) in this paper (Petters and Kreidenweis, 2013; Sullivan et al., 2009).

The hygroscopic parameter \(\kappa_{AMS}\) can be obtained from AMS measurements using

\[
\kappa_{AMS} = \kappa_{org} \times f_{org} + \kappa_{inorg} \times f_{inorg}
\]

where \(f_{org}\) and \(f_{inorg}\) are the organics and inorganics volume fraction derived from AMS measurements (Petters and Kreidenweis, 2007). Bulk \(\kappa_{AMS}\) (hereafter \(\kappa_{AMS,B}\)) and size-resolved \(\kappa_{AMS}\) (hereafter \(\kappa_{AMS,SR}\)) are obtained from the corresponding bulk and size-resolved volume
fractions of organics and inorganics, respectively. Also, it was assumed that \( \kappa_{\text{inorg}} = 0.6 \) for the whole campaign, \( \kappa_{\text{org}} = 0.2 \) for the hazy period and \( \kappa_{\text{org}} = 0.1 \) for the foggy and non-episode periods.

The time-series hygroscopicities derived from bulk and size-resolved AMS measurements are shown in Fig.S2. \( \kappa_{\text{AMS,b}} \) were larger than \( \kappa_{\text{AMS,SR}} \) in all four SS because bulk AMS compositions biased towards the inorganics as discussed below. Their difference increases as SS increases because the corresponding \( D_{50} \) decreases and these smaller particles have a larger difference in organic fraction than the bulk has.

3 Results and discussion

3.1 Overview

Fig.2 shows an overview of the bulk \( N_{\text{CCN}} \) concentrations and \( N_{\text{CCN}}/N_{\text{CN}} \) activation ratio at SS of (a) 0.15\%, (b) 0.35\%, (c) 0.50\%, and (d) 0.70\%, as well as (e) the bulk \( N_{\text{CN}} \) and the NR-PM1 total and component mass concentration and (f) the volume fractions of the AMS chemical components over the entire month of May 2011. Statistics of the measurements are given in Table I. The gaps in the data in Fig.2 are due to instrument downtime. For most of the time, the total \( N_{\text{CCN}} \) at SS of 0.15\%, 0.35\%, 0.50\% and 0.70\% were below 800 cm\(^{-3} \), 3000 cm\(^{-3} \), 5000 cm\(^{-3} \) and 5600 cm\(^{-3} \) respectively, and \( N_{\text{CN}} \) was below 10000 cm\(^{-3} \). Both \( N_{\text{CCN}} \) and \( N_{\text{CN}} \) in this study are lower than those observed in July 2006 in Guangzhou (Rose et al., 2010). Large fluctuations in the bulk \( N_{\text{CCN}}/N_{\text{CN}} \) ratios were also observed. The bulk \( N_{\text{CCN}}/N_{\text{CN}} \) ratio was as low as 0.03 at SS = 0.15\%, but it was as high as 0.92 at SS = 0.70\%. Even at the same SS, the bulk \( N_{\text{CCN}}, N_{\text{CN}} \) and \( N_{\text{CCN}}/N_{\text{CN}} \) ratio varied greatly during the campaign.

The bulk mass concentrations of NR-PM1 ranged from 0.8 \( \mu \text{g m}^{-3} \) to 72.4 \( \mu \text{g m}^{-3} \) with a mean value of 14.5 \( \pm \) 9.7 \( \mu \text{g m}^{-3} \) as shown in Fig.2e. The average bulk volume fractions of NR-species were 53 \( \pm \) 10\%, 25 \( \pm \) 13\%, 18 \( \pm \) 4\%, 4 \( \pm \) 3\% for sulfate, organics, ammonia, and nitrate, respectively (Lee et al., 2013). The bulk mass concentrations for all NR-species were in general
low during the campaign compared with those reported for the PRD region (Gong et al., 2012; Rose et al., 2011; Takegawa et al., 2009; Xiao et al., 2011).

There were two periods of particular interest during this campaign: one was a foggy period (May 15) and the other was a hazy period (May 28-30). The division of the month of May in 2011 into foggy, hazy and non-episode periods was based on differences in meteorology, such as RH, temperature and cloud cover, and mass concentration and the O:C ratio. On average, the foggy period had a high RH (91.1%), a low temperature (23.3 °C) and a high percentage cloud coverage (89.7%) and a high liquid water content (LWC) in fine particles (47.5 μg m⁻³) as shown in Li et al. (2013). The hazy period had a much lower RH (66.6%), a higher temperature (26.2 °C) and a much lower percentage cloud coverage (43.3%) and LWC (17.5 μg m⁻³). The slowing surface winds and the establishment of a well-defined land-sea breeze with a gradual daily reversal of wind direction contributed to the accumulation of local and regional pollutants coming from the PRD due to the persistent northerly and northwesterly air masses (Lee et al., 2013).

During the foggy period, the bulk NR-PM1 was as high as 30 μg m⁻³ (Fig. 2e; Li et al., 2013). The hazy period was much less humid and it saw the highest mass concentration of NR-PM1 species recorded during the whole campaign. The highest degree of oxygenation with average O:C ratio of 0.51 was also obtained (Li et al., 2013). During the hazy period, the mean bulk $N_{CCN}$ ranged from 1100 cm⁻³ with bulk $N_{CCN}/N_{CN}$ of 0.22 at SS = 0.15% to 5300 cm⁻³ with bulk $N_{CCN}/N_{CN}$ of 0.72 at SS = 0.70%. During non-episode periods, the mean bulk $N_{CCN}$ ranged from 300 cm⁻³ with bulk $N_{CCN}/N_{CN}$ of 0.14 at SS = 0.15% to 2700 cm⁻³ with bulk $N_{CCN}/N_{CN}$ of 0.61 at SS = 0.70%.

### 3.2 $\kappa_{CCN}$ and $\kappa_{AMS}$

The average size-resolved mass distributions and volume fractions ($f$) of NR-PM1 calculated from AMS measurements are shown in Fig.3a-c and Fig.3d-f, respectively, for the foggy period, the hazy period, and the non-episode periods. The NR-PM1 showed a major mode at the dry
particle size ($D_m$, hereafter, diameters shown are $D_m$) of ~285 nm in the foggy period, at ~355 nm in the hazy period and at ~325 nm in the non-episode periods. Sulfate and organics accounted for large mass fractions (78% in total) during the whole campaign as shown in Table II. Sulfate dominated in the foggy period, contributing to a volume fraction of 0.45 for 42-200 nm particles. Organics and nitrate often had a shoulder at a small size mode at 100 nm to 130 nm. This shoulder was obvious in the hazy period and non-episode periods but not so in the foggy period. On average, this smaller mode accounted for 11% and 12% of organics and nitrate, respectively. On the other hand, only 2% of sulfate was found in this mode (Lee et al., 2013).

Fig. 3d-f show the average size-resolved volume fraction distributions of the AMS aerosol compositions from 42 nm to 200 nm in the foggy period, the hazy period and the non-episode periods. The volume fraction of organics decreased while the inorganics increased with particle size. Overall, the size-resolved volume fractions of organics ranged from 0.73 at 42 nm to 0.25 at 200 nm. Additionally, the bulk volume ratio of organics to inorganics between 42 nm and 200 nm was 0.65 in the foggy period, 1.33 in the hazy period, and 0.87 in the non-episode periods.

The measured $\kappa_{CCN}$ (yellow symbols) and the calculated $\kappa_{AMS,SR}$ (blue symbols), in the form of median values and interquartile ranges, are plotted against their corresponding $D_{50}$ in Fig.3d-f. The median and mean values of $\kappa_{CCN}$ and $\kappa_{AMS,SR}$ were essentially the same. Overall, the median $D_{50}$ were 116 nm, 68 nm, 55 nm, and 47 nm, with an interquartile range of less than 16%, at SS of 0.15%, 0.35%, 0.50%, and 0.70%, respectively. During the foggy period, which featured high inorganics volume fractions, the median $\kappa_{CCN}$ were 0.44, 0.37, 0.36 and 0.29 at SS from 0.15% to 0.70%. They are higher than the corresponding values in the hazy period (0.38, 0.36, 0.32 and 0.28) and the non-episode periods (0.39, 0.37, 0.33 and 0.27). The difference in $\kappa_{CCN}$ was most obvious at SS = 0.15%, at which $D_{50}$ was around 110 nm, and the corresponding inorganic volume fraction was 0.6 in foggy period, 0.4 in the hazy period and 0.5 in the non-episode period. The high inorganic volume fraction results in high aerosol hygroscopicity.

The $\kappa_{AMS,SR}$ calculated from Equation 3 assuming $\kappa_{org} = 0.1$ and $\kappa_{inorg} = 0.6$ agreed well with the measured $\kappa_{CCN}$ in the foggy period and the non-episode periods as shown in Fig. 3d and f. In the hazy period (Fig.3e), assuming $\kappa_{org} =0.2$ and $\kappa_{inorg} = 0.6$ gave better agreement between
\( \kappa_{\text{AMS,SR}} \) and \( \kappa_{\text{CCN}} \). The hazy period had a higher O:C ratio of 0.51, compared to 0.43 and 0.39 in foggy and the non-episode periods respectively (Li et al., 2013), leading to a higher hygroscopicity of the organic aerosols (Chang et al., 2010; Lambe et al., 2011; Massoli et al., 2010; Mei et al., 2013; Moore et al., 2012b).

We further examine the correlations between the observed \( \kappa_{\text{CCN}} \) and the size-resolved organic volume fraction \( f_{\text{org}} \) in Fig.4a for the hazy period and Fig.4b for the rest of the campaign. In order to avoid the negatively impact of low signal-to-noise ratios of AMS measurements on the correlation study, only data points with mass concentrations in a size bin of larger than 0.6 \( \mu g \) m\(^{-3}\) were used. Extrapolation of the least square fit line in Fig.4a and Fig.4b to \( f_{\text{org}} = 1 \) yields \( \kappa_{\text{org}} = 0.21 \pm 0.02 \) and 0.09 \pm 0.01 for the organic fraction and extrapolation to \( f_{\text{org}} = 0 \) yields \( \kappa_{\text{inorg}} = 0.59 \pm 0.03 \) and 0.59 \pm 0.01 for the inorganic fraction, respectively. These values are close to the characteristic values of organic (0.1) and inorganic hygroscopicity (0.6) in the PRD region (Rose et al., 2011), and to the averaged values of \( \kappa_{\text{org}} = 0.1 \) and \( \kappa_{\text{inorg}} = 0.6 - 0.7 \) in earlier studies in Beijing and the Gulf of Mexico (Gunthe et al., 2011; Moore et al., 2012b). The average organic hygroscopicity is within the typical range for individual organic species from zero for insoluble organics to 0.3 for soluble organics (Hersey et al., 2011; Lambe et al., 2011; Petters and Kreidenweis, 2007). \( \kappa_{\text{AMS,SR}} \) correlates reasonably well with \( \kappa_{\text{CCN}} \), with \( R^2 \) of 0.51, as shown in Fig.S3.

On the other hand, the mean value of \( \kappa_{\text{AMS,B}} \) derived from bulk AMS compositions was 0.45 at \( SS = 0.15\% \) and 0.46 for the other \( SS \), which are significantly larger than the measured \( \kappa_{\text{CCN}} \) ranging from 0.39 to 0.28 for \( SS \) of 0.15\% to 0.7\% as shown in Table IV. Size-resolved AMS measurements are needed to accurately determine the hygroscopicity parameter and predict \( N_{\text{CCN}} \) (Cubison et al., 2008; Moore et al., 2012a). For closure analysis shown below, we use \( \kappa_{\text{org}} = 0.1 \) and \( \kappa_{\text{inorg}} = 0.6 \).

### 3.3 CCN closure study
The closure studies on $N_{\text{CCN}}$ prediction were carried out based on the measured size-resolved $N_{\text{CN}}$ distributions and the AMS measurements. In the first approach, we assumed internal mixing and used $\kappa_{\text{AMS}}$ from (i) bulk and (ii) the size-resolved AMS measurements for each dataset in Equation 3, and (iii) assumed constant $\kappa$ values. The corresponding individual $D_{50}$ was then calculated from these $\kappa$ estimates using Equation 2, based on which $N_{\text{CCN}}$ was predicted. Furthermore, we also used the average $D_{50}$ over the whole campaign in $N_{\text{CCN}}$ prediction. Table III summarizes the assumptions and parameters used in these methods. In these cases $N_{\text{CCN}}$ was calculated by integrating the measured size-resolved $N_{\text{CN}}$ distributions for particles larger than $D_{50}$. The aim of using the average $D_{50}$ was to test how well it represented the activation properties of aerosol during the campaign. Finally, we examined the relative importance of hygroscopicity and mixing state in $N_{\text{CCN}}$ predictions at different SS by comparing the $N_{\text{CCN}}$ using the average $D_{50}$ with an internal mixing assumption and the size-resolved CCN activation ratios from CCN measurements which reflect the actual mixing state of the aerosols. The last approach involved integrating the product of the measured size-distribution of $N_{\text{CN}}$ and the size-resolved CCN activation ratio in each particle size bin.

### 3.3.1 Prediction of $N_{\text{CCN}}$ based on $\kappa_{\text{AMS}}$

#### 3.3.1.1 $\kappa_{\text{AMS}}$ from bulk AMS measurements

The hygroscopicity $\kappa_{\text{AMS,B}}$ was estimated by assuming that all particles have the same chemical composition as determined by bulk AMS measurements and $\kappa_{\text{org}} = 0.1$ and $\kappa_{\text{inorg}} = 0.6$. The closure results are shown in Fig.5i a-h and Table IV. Overall, the approaches of using individual $D_{50}$ and the average $D_{50}$ grossly over-predicted $N_{\text{CCN}}$ by up to 21% and 26%, respectively. As shown in Fig.3a-c, PM1 was dominated by inorganic species with the bulk volume fraction as high as 69% during the whole period. The bulk volume ratio mainly reflects the composition of particles from 200 to 500 nm where inorganic species dominated. On the other hand, $D_{50}$ at the four SS were all less than 200 nm where organic species accounted for more than 39% of bulk volume fraction as shown in Table II and Fig.3. Therefore, deriving $\kappa_{\text{AMS}}$ from bulk AMS measurements leads to a positive bias toward inorganic species, and hence an
overestimation of \( \kappa_{\text{AMS,B}} \) and \( \mathcal{N}_{\text{CCN}} \). Wang et al. (2010) found that the overestimation arising from the use of the bulk mass concentrations decreased from 80% to 39% when \( SS \) decreased from 0.35% to 0.11%. Our data also shows decreasing overestimation as \( SS \) decreases, except for data at \( SS = 0.15\% \), where the \( \mathcal{N}_{\text{CCN}} \) was smaller than 1000 cm\(^{-3}\) most of the time. The low counts may have introduced larger uncertainty in the measurements as shown in SI.

### 3.3.1.2 \( \kappa_{\text{AMS}} \) from size-resolved AMS measurements

Fig.5ii a-d and e-h show the correlations between the measured \( \mathcal{N}_{\text{CCN}} \) and the \( \mathcal{N}_{\text{CCN}} \) predicted from the individual \( D_{50} \) of each data set and the averaged \( D_{50} \) derived from \( \kappa_{\text{AMS,SR}} \), respectively. The slope and \( R^2 \) are given in Table IV. In general, the \( \mathcal{N}_{\text{CCN}} \) prediction deviated by 10% or less for both approaches and the average \( D_{50} \) adequately reflects the aerosol activation properties. At \( SS = 0.70\% \), individual \( D_{50} \) and the average \( D_{50} \) gave the close deviations of 10% and 9% respectively between the measured and predicted \( \mathcal{N}_{\text{CCN}} \). At high \( SS \), where even particles of moderate hygroscopicity are activated (Kim et al., 2011), the \( \mathcal{N}_{\text{CCN}} \) prediction is less sensitive to hygroscopicity than at low \( SS \). The difference of the deviations increased as \( SS \) decreased from 0.70% to 0.35%. At lower \( SS \), differences in hygroscopicity as reflected from the different \( D_{50} \) used in the calculations gave larger differences in \( \mathcal{N}_{\text{CCN}} \) predictions.

The overestimation from using the average \( D_{50} \) decreased from 9% at \( SS \) of 0.70% \( (D_{50} = 46 \text{ nm}) \) to 5% and 1% at \( SS \) of 0.50% \( (D_{50} = 56 \text{ nm}) \) and 0.35% \( (D_{50} = 67 \text{ nm}) \), respectively. The fraction of non/less-hygroscopic hydrocarbon-like organic aerosols (HOA) decreased with increasing particle size (Lee et al., 2013). They contribute little to \( \mathcal{N}_{\text{CCN}} \) by themselves but the assumption of internal mixing allows them to contribute to CCN due to their mixing with more hygroscopic species and leads to an overestimated \( \mathcal{N}_{\text{CCN}} \) (Rose et al., 2011; Wang et al., 2010). Size-resolved EC was not available and EC might also have caused the overestimation in \( \mathcal{N}_{\text{CCN}} \) prediction. When \( SS \) decreased, \( D_{50} \) increased and the impact of HOA on the \( \mathcal{N}_{\text{CCN}} \) predictions decreased because of their smaller abundance relative to the hygroscopic inorganics. The large deviation in \( \mathcal{N}_{\text{CCN}} \) prediction at \( SS = 0.15\% \) may be due to the uncertainty in the low number
counts of CCN measurements or the high sensitivity of $N_{CCN}$ to hygroscopicity at low $SS$ as discussed later.

### 3.3.2 Prediction of $N_{CCN}$ from the constant $\kappa$

A constant $\kappa = 0.30$ has been proposed for predicting $N_{CCN}$ and understanding the indirect effects of continental aerosols on climate on a global modeling scale (Andreae and Rosenfeld, 2008; Pringle et al., 2010). Rose et al. (2011) showed that the deviations between the measured and predicted $N_{CCN}$ were less than 20% when they used an averaged $\kappa = 0.30$ over the course of their campaign in PRD in 2006. We evaluated the use of constant $\kappa = 0.30$, 0.33 (the average $\kappa_{AMS,SR}$ over the campaign at the four $SS$), and 0.35 to estimate $N_{CCN}$. Overall, using $\kappa = 0.35$ overestimated $N_{CCN}$ at all four $SS$ while using 0.33 and 0.30 underestimated it at low $SS \leq 0.35\%$ and overestimated it at high $SS \geq 0.50\%$, respectively, as shown in Fig.S4 and Table IV. The slopes for $\kappa = 0.30$, 0.33 and 0.35 are quite different (0.91, 0.98 and 1.05) at $SS = 0.15\%$, while they are much closer (1.11, 1.12 and 1.13) at $SS = 0.70\%$. The difference in $N_{CCN}$ prediction for the three $\kappa$ decreased gradually from 14% at $SS = 0.15\%$ to 2% at $SS = 0.70\%$. These results further confirm that the prediction of $N_{CCN}$ is less sensitive to $\kappa$ at high $SS$ than at low one, and that the impact of hygroscopicity on the $N_{CCN}$ prediction decreases with increasing $SS$.

The difference in the sensitivity of predicted $N_{CCN}$ to hygroscopicity at different $SS$ can also be attributed to the aerosol size distributions (Dusek et al., 2006; Ervens et al., 2007). The average aerosol size distribution over the whole period had a main mode at ~70 nm and a shoulder at ~30 nm (Fig.6a) in this campaign. At $SS = 0.15\%$, $D_{50}$ is approximately 116 nm and on the right of the main mode (Fig.6b), a slight variation of $\kappa$ and $D_{50}$ will cause a large change in $N_{CCN}$ prediction. On the contrary, at $SS = 0.70\%$, the corresponding $D_{50} = 46$ nm is on the left of the main mode (Fig.6c), a variation of $\kappa$ and $D_{50}$ will have less impact on $N_{CCN}$ prediction as the $N_{CCN}$ is dominated by the mode at 70 nm.

In addition, we carried out the $N_{CCN}$ prediction during the hazy period, when HOA contributes to ~25% of OA (Li et al, 2013), based on the average size-resolved (1) $\kappa_{AMS} = 0.33$
over the whole campaign period and (2) $\kappa_{\text{AMS}} = 0.35$ over the hazy period only. As shown in Fig. S5, using $\kappa_{\text{AMS}} = 0.33$ and 0.35 gave similar results with overestimations of 14% and 13% at $SS = 0.70\%$ respectively. In the hazy period, the assumption of internal mixing state allowed HOA containing particles to act as CCN, thereby resulting in an overestimation of $N_{\text{CCN}}$ by up to 14%. At $SS = 0.15\%$, using $\kappa = 0.33$ led to an overestimation of just 2%, while an overestimation of 9% was found when using $\kappa = 0.35$. Overall, using $\kappa = 0.33$ gave predictions of $N_{\text{CCN}}$ (Table IV) comparable to those using the $\kappa_{\text{AMS,SR}}$ and better than those using $\kappa_{\text{AMS,B}}$ at all four $SS$.

### 3.3.3 Mixing state and hygroscopicity

As discussed earlier, closure analysis based on hygroscopicity or $D_{50}$ derived from chemical compositions alone cannot account for variability in the mixing state of aerosols, which could cause significant differences between predicted and measured $N_{\text{CCN}}$. In this section, we first calculate $N_{\text{CCN}}$ by integrating the measured size-resolved $N_{\text{CN}}$ distributions above the average $D_{50}$, obtained from the average CCN size-resolved activation ratio over the whole campaign. The second method involves integrating the product of the measured size-distribution of $N_{\text{CN}}$ and the average size-resolved $N_{\text{CCN}}/N_{\text{CN}}$ activation ratio in each particle size bin. The size-resolved $N_{\text{CCN}}/N_{\text{CN}}$ activation ratios reflect the influences of both the size-resolved chemical compositions and mixing state on CCN activity, and thus can potentially exclude the impact of non/less hygroscopicity species on $N_{\text{CCN}}$ prediction and be used to examine the relative importance of mixing state and hygroscopicity in closure analysis compared to predictions assuming internal mixing state (Deng et al., 2013). The first method involves the hygroscopicity of aerosols as reflected by the value of $D_{50}$ and the assumption of internal mixing while the second method involves hygroscopicity with actual mixing state information imbedded in the measured activation ratio curves. A comparison of the predictions of these two methods would give hints to the role of assumption of mixing states. The average size-resolved CCN activation ratios at the four $SS$ over the whole campaign are shown in Fig.S6. Data points are shown as means ± standard deviations.
The correlations of measured and predicted $N_{\text{CCN}}$ based on the average $D_{50}$ (a-d) and the average size-resolved activation ratio (e-h) are shown in Fig. 5 iii a-d and e-h. The slopes of the fitted lines and $R^2$ at different SS are given in Table IV. The predicted and the measured $N_{\text{CCN}}$ differed by less than 10% using the average $D_{50}$. The difference is comparable to those using the average $D_{50}$ from $\kappa_{\text{AMS,SR}}$ (Fig. 5ii e-h). At $SS = 0.70\%$, using the average size-resolved CCN activation ratios reduced the overestimation from 8% when using the average $D_{50}$ to 4%. As discussed above, the sensitivity of the $N_{\text{CCN}}$ prediction to hygroscopicity is low at $SS = 0.70\%$, where a large change of 25% in hygroscopicity from 0.28 to 0.35 result in only a variation within 5% in $N_{\text{CCN}}$ (Table IV). From the AMS measurements, the portion of non/less-hygroscopic species inferred by the fractions of $f_{43}$ and $f_{57}$ increased as the particle size decreased (Lee et al., 2013). Because of their higher abundance, their mixing with the hygroscopic components has a higher impact at $SS = 0.70\%$ ($D_{50} = 46$ nm) than that at low $SS = 0.15\%$ ($D_{50} = 116$ nm), where the reduction in the overestimation is minimal, from 10% when using the average $D_{50}$ to 9% when using the average activation ratios approach. On the contrary, a difference of 19% was found when hygroscopicity increased from 0.30 to 0.39 at this low SS.

The average size-resolved activation ratios during the hazy, foggy and non-episode periods at $SS=0.15\%$ and 0.7% are shown in Fig. 7. At $SS=0.15\%$, the activation ratios during the hazy and non-episode periods are similar but it is higher during the foggy period due possibly to the higher volume fraction of inorganics (Fig. 3d-f) and the smaller amount of non/less hygroscopic organics (Li et al., 2013). At $SS=0.70\%$, the CCN activation ratios of particles ranging from 50 nm to 100 nm in size are lower in the hazy period than in the non-episode period. The difference in the trends at $SS=0.15\%$ and 0.70% may be due to the larger fractions of non/less hygroscopic species in smaller particles in the hazy period. These particles, which constitute a larger fraction of OA in the hazy period than in the other periods, likely formed external mixtures containing the aged particles of sulfate and the more oxidized (and hygroscopic) organics. Hence, a larger difference in the activation ratios between the hazy and the other periods could be observed at $SS=0.70\%$ than at $SS=0.15\%$. 

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Fig. 8 shows the $N_{CCN}$ predicted based on the average $D_{50}$ and the average size-resolved CCN activation ratio over the hazy period. At $SS = 0.15\%$, using the average CCN activation ratio reduces overestimation from 12\% when using average $D_{50}$ to 10\%. However, a much larger reduction from 8\% to 1\% was found at $SS = 0.70\%$. This comparison further suggests that a change in mixing state affects $N_{CCN}$ prediction more at high $SS$ than at the low $SS$ and that $N_{CCN}$ prediction is more sensitive to mixing state at high $SS$ than hygroscopicity.

4 Conclusion

In this study, a DMT CCNe-200 for $N_{CCN}$ measurement, a TSI SMPS for $N_{CN}$ measurement, and an Aerodyne HR-ToF-AMS for size-resolved and bulk PM1 chemical composition measurement were used to investigate the size-resolved CCN activity at a coastal site in Hong Kong in May 2011. Closure studies were carried out based on the $\kappa_{AMS}$ estimated from bulk and size-resolved AMS measurement assuming internal mixing state. The deviation of $N_{CCN}$ predicted from the individual $D_{50}$ obtained from $\kappa_{AMS}$ was similar to that predicted from the average $D_{50}$ over the whole period at the four $SS$, which indicates that the average $D_{50}$ well represented the aerosol CCN activation properties in this study. Using $\kappa_{AMS,B}$ grossly over-predicted $N_{CCN}$ by up to 26\% because of the positive bias toward the inorganic fraction. On the contrary, the $N_{CCN}$ prediction based on $\kappa_{AMS,SR}$ was within 10\% of the measurements. An accurate description of $\kappa$ incorporating size-dependent compositions is necessary for good $N_{CCN}$ predictions.

We compared the sensitivity of the $N_{CCN}$ prediction to hygroscopicity (based on assumed internal mixing and $\kappa$ estimates) and mixing state at different $SS$. $N_{CCN}$ was found to be more sensitive to hygroscopicity than to mixing state at $SS = 0.15\%$ but the reverse is true at $SS = 0.70\%$. At $SS = 0.15\%$, $D_{50}$ (116nm) is larger than the mode diameter of the typical aerosol distributions we observed. A slight variation in $\kappa$ (and $D_{50}$) would have a larger effect on $N_{CCN}$ prediction than would at high $SS = 0.70\%$, where $D_{50}$ (46 nm) is smaller than the mode diameter. The effect of mixing state is larger at $SS = 0.70\%$, which is associated with smaller particles
having a higher percentage of non/less-hygroscopic components, than at $SS = 0.15\%$.

Hygroscopicity is relatively less important to $N_{\text{CCN}}$ prediction at this high $SS$.

5 Acknowledgments

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References


Kim, J. H., Yum, S. S., Shim, S., Yoon, S.-C., Hudson, J. G., Park, J., and Lee, S.-J.: On aerosol hygroscopicity, cloud condensation nuclei (CCN) spectra and critical supersaturation measured


Sueper, D.: ToF-AMS data analysis software: http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html, (last access: 1 June, 2012), 2011.


Table I. Statistics of the bulk $N_{CCN}$ (cm$^{-3}$) at four SS (%) showing the minimum, maximum, mean number concentration, the $N_{CCN}/N_{CN}$ ratio, and standard deviation (SD). The last column shows the number of samples ($n$) in this campaign.

<table>
<thead>
<tr>
<th>SS (%)</th>
<th>Max $N_{CCN}$ (cm$^{-3}$)</th>
<th>Min $N_{CCN}$ (cm$^{-3}$)</th>
<th>$N_{CCN}/N_{CN}$</th>
<th>$N_{CCN}/N_{CN}$</th>
<th>Mean $N_{CCN}$ (cm$^{-3}$)</th>
<th>$N_{CCN}/N_{CN}$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>2815</td>
<td>33</td>
<td>0.54</td>
<td>0.03</td>
<td>512 $\pm$ 452</td>
<td>0.16 $\pm$ 0.08</td>
<td>319</td>
</tr>
<tr>
<td>0.35</td>
<td>8055</td>
<td>186</td>
<td>0.78</td>
<td>0.08</td>
<td>1546 $\pm$ 1137</td>
<td>0.48 $\pm$ 0.14</td>
<td>316</td>
</tr>
<tr>
<td>0.50</td>
<td>9156</td>
<td>210</td>
<td>0.82</td>
<td>0.12</td>
<td>1815 $\pm$ 1285</td>
<td>0.57 $\pm$ 0.14</td>
<td>326</td>
</tr>
<tr>
<td>0.70</td>
<td>9268</td>
<td>280</td>
<td>0.92</td>
<td>0.16</td>
<td>2082 $\pm$ 1484</td>
<td>0.65 $\pm$ 0.14</td>
<td>320</td>
</tr>
</tbody>
</table>
Table II. The average size-resolved mass concentrations (µg m\(^{-3}\), Conc.) and volume fractions (f) of chemical compositions from size-resolved AMS measurements during the foggy, hazy and the non-episode periods. Conc. and f were obtained by integrating over the size range (\(D_m\)) from 42 nm to 1200 nm for Fig.3a-c and from 42 nm to 200 nm for Fig.3d-f. Data are shown as mean ± standard deviations.

<table>
<thead>
<tr>
<th>Period</th>
<th>Organics</th>
<th>Sulfate</th>
<th>Ammonium</th>
<th>Nitrate</th>
<th>Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc.</td>
<td>f</td>
<td>Conc.</td>
<td>f</td>
<td>Conc.</td>
</tr>
<tr>
<td>Foggy</td>
<td>1.60 ± 1.10</td>
<td>0.39 ± 0.12</td>
<td>4.86 ± 3.51</td>
<td>0.45 ± 0.10</td>
<td>1.33 ± 0.98</td>
</tr>
<tr>
<td>Hazy</td>
<td>4.25 ± 2.52</td>
<td>0.57 ± 0.08</td>
<td>5.96 ± 4.36</td>
<td>0.29 ± 0.06</td>
<td>1.71 ± 1.22</td>
</tr>
<tr>
<td>The rest</td>
<td>1.19 ± 0.71</td>
<td>0.47 ± 0.11</td>
<td>2.65 ± 1.86</td>
<td>0.37 ± 0.08</td>
<td>0.81 ± 0.55</td>
</tr>
</tbody>
</table>
Table III. Methods used in $N_{CCN}$ prediction based on the individual and average $D_{50}$ over whole period from AMS measurement.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Mixing state</th>
<th>Chemical composition</th>
<th>$\kappa_{AMS}$</th>
<th>$D_{50}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Internal</td>
<td>Bulk AMS measurements</td>
<td></td>
<td>Individual</td>
</tr>
<tr>
<td>II</td>
<td>Internal</td>
<td>Bulk AMS measurements</td>
<td>$\kappa_{AMS} = 0.1 \times f_{\text{org}} + 0.6 \times f_{\text{inorg}}$</td>
<td>Average</td>
</tr>
<tr>
<td>III</td>
<td>Internal</td>
<td>Size-resolved AMS measurements</td>
<td></td>
<td>Individual</td>
</tr>
<tr>
<td>IV</td>
<td>Internal</td>
<td>Size-resolved AMS measurements</td>
<td></td>
<td>Average</td>
</tr>
<tr>
<td>V</td>
<td>Internal</td>
<td>N/A</td>
<td>0.35/0.33/0.30</td>
<td>Constants</td>
</tr>
</tbody>
</table>
Table IV. Overview of $N_{CCN}$ predictions, $\kappa$ from $D_{50}$ based on CCN measurement and derived from equation 3 based on AMS measurement are shown as mean ± standard deviation, slope and $R^2$ are from the least square fit between the calculated $N_{CCN}$ and measured ones.

<table>
<thead>
<tr>
<th>Categories</th>
<th>Principles</th>
<th>SS (%)</th>
<th>$\kappa$</th>
<th>Slope</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCN_C</td>
<td>The average $D_{50}$ from CCN measurement</td>
<td>0.15</td>
<td>0.39 ± 0.06</td>
<td>1.10</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.36 ± 0.09</td>
<td>1.01</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>0.31 ± 0.10</td>
<td>1.05</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>0.28 ± 0.09</td>
<td>1.08</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>The average CCN activation ratio</td>
<td>0.15</td>
<td>-</td>
<td>1.09</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>-</td>
<td>0.99</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>-</td>
<td>1.02</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>-</td>
<td>1.04</td>
<td>0.98</td>
</tr>
<tr>
<td>AMS</td>
<td>The $D_{50}$ from $\kappa_{AMS_B}$</td>
<td>0.15</td>
<td>-</td>
<td>1.21</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>-</td>
<td>1.06</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>-</td>
<td>1.13</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>-</td>
<td>1.17</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>The average $D_{50}$ from $\kappa_{AMS_B}$</td>
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<td>0.45 ± 0.07</td>
<td>1.26</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.46 ± 0.06</td>
<td>1.08</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>0.46 ± 0.06</td>
<td>1.13</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>0.46 ± 0.07</td>
<td>1.18</td>
<td>0.98</td>
</tr>
<tr>
<td>Others</td>
<td>The $D_{50}$ from $\kappa_{AMS_S}$</td>
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<td>-</td>
<td>1.06</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>-</td>
<td>0.94</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>-</td>
<td>1.03</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>-</td>
<td>1.10</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>The average $D_{50}$ from $\kappa_{AMS_S}$</td>
<td>0.15</td>
<td>0.37 ± 0.07</td>
<td>1.08</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.35 ± 0.08</td>
<td>1.01</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>0.31 ± 0.07</td>
<td>1.05</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>0.29 ± 0.09</td>
<td>1.09</td>
<td>0.98</td>
</tr>
<tr>
<td>Constant $\kappa$</td>
<td></td>
<td>0.15</td>
<td>0.35/0.33/0.30</td>
<td>1.05/0.98/0.91</td>
<td>0.95/0.95/0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>0.35/0.33/0.30</td>
<td>1.01/0.96/0.91</td>
<td>0.95/0.95/0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50</td>
<td>0.35/0.33/0.30</td>
<td>1.08/1.05/1.03</td>
<td>0.97/0.97/0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>0.35/0.33/0.30</td>
<td>1.13/1.12/1.11</td>
<td>0.98/0.98/0.98</td>
</tr>
</tbody>
</table>
**Figure Captions**

Fig. 1. Schematic of the experimental setup for size-resolved CCN activation and chemical composition measurement.

Fig. 2. The $N_{CCN}$ and the $N_{CCN}/N_{CN}$ ratio at SS of (a) 0.15%, (b) 0.35%, (c) 0.50%, and (d) 0.70%; (e) $N_{CN}$ and NR-species mass concentrations from CCNc, SMPS and AMS; (f) NR-species volume fractions derived from AMS.

Fig. 3. Size-resolved mass concentration distributions of aerosol chemical composition derived from AMS averaged over (a) the foggy period, (b) the hazy period, and (c) the non-episode periods; the corresponding size-resolved volume fractions of aerosol chemical compositions (colored areas), the observed $\kappa_{CCN}$ (yellow) and the calculated $\kappa_{AMS,SR}$ (blue) during (d) the foggy period, (e) the hazy period and (g) the non-episode period. Data points median values and interquartile ranges. $\kappa_{inorg} = 0.6$ in all cases, $\kappa_{org} = 0.1$ in (d) and (f), $\kappa_{org} = 0.2$ in (e).

Fig. 4. Correlations between the observed $\kappa_{CCN}$ and the organic volume fraction ($f_{org}$) determined by size-resolved AMS measurements for the (a) hazy period ($n = 72$) and (b) the non-episode period ($n = 516$). The red line is the linear least squares fit (p-value < 0.01) shown in figure.

Fig. 5. Calculations of $N_{CCN}$ based on i (a-d) the individual $D_{50}$ and (e-h) the average $D_{50}$ over the whole period from $\kappa_{AMS,B}$, ii (a-d) the individual $D_{50}$ and (e-h) the average $D_{50}$ over the whole period from $\kappa_{AMS,SR}$ and iii (a-d) the average $D_{50}$ and (e-h) the average size-resolved CCN activation ratio from CCN measurement over the whole period.

Fig. 6. The average aerosol size distribution over the whole period (a), $N_{CCN}$ prediction based on $D_{50}$ at SS of (b) 0.15% and (c) 0.70%. Data points are mean values and standard deviation.

Fig. 7. The average size-resolved CCN activation ratio at SS of (a) 0.15% and (b) 0.70% during the hazy, foggy and non-episode periods.

Fig. 8. $N_{CCN}$ estimation in hazy period based on (a and b) the average $D_{50}$ and (c and d) the average size-resolved CCN activation ratio from CCN measurement over the hazy period.
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