Atmos. Chem. Phys. Discuss., 14, 9067–9107, 2014 www.atmos-chem-phys-discuss.net/14/9067/2014/ doi:10.5194/acpd-14-9067-2014 © Author(s) 2014. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Cloud condensation nuclei (CCN) and HR-ToF-AMS measurements at a coastal site in Hong Kong: size-resolved CCN activity and closure analysis

J. W. $Meng^1$, M. C. $Yeung^2$, Y. J. Li^1 , B. Y. L. Lee^1 , and C. K. $Chan^{1,2}$

¹Division of Environment, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong SAR, China

²Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology Clear Water Bay, Hong Kong SAR, China

Received: 6 March 2014 - Accepted: 10 March 2014 - Published: 3 April 2014

Correspondence to: C. K. Chan (keckchan@ust.hk)

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



Abstract

The cloud condensation nuclei (CCN) properties of atmospheric aerosols were measured on 1–30 May 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 %, and 0.70 % were 116 nm, 67 nm, 56 nm, and 46 nm, respectively. The corresponding average hygroscopic parameters (κ_{CCN}) were 0.39, 0.36, 0.31, and 0.28. The decrease in κ_{CCN} can be attributed to the increase in organic to inorganic volume ratio as particle size decreases, as mea-

- sured by an Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-¹⁵ ToF-AMS). The κ_{CCN} correlates reasonably well with κ_{AMS} based on size-resolved AMS
- measurements: $\kappa_{AMS} = \kappa_{org} \times f_{org} + \kappa_{inorg} \times f_{inorg}$, 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, $N_{\rm CCN}$ was estimated by integrating the measured size-resolved $N_{\rm CN}$ for particles larger than D_{50} derived from κ assuming internal mixing state. Esti-²⁰ mates using $\kappa_{\rm AMS}$ from size-resolved AMS measurements 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 κ_{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 con-
- stant $\kappa = 0.33$ (the average value of size-resolved κ_{AMS} 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.

- ¹⁰ 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 $N_{\rm CCN}$ (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 (κ) is used to represent the effect of chemical composition on CCN activ-
- ¹⁵ ity (Petters and Kreidenweis, 2007, 2013). Size-resolved chemical compositions give a size-dependent κ which leads to better $N_{\rm CCN}$ 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

- ²⁰ 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
- ²⁵ internal mixing are usually larger than measured values by 20% or even more, since this assumption overestimates the contribution of organics to $N_{\rm CCN}$ (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 κ (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 $N_{\rm CCN}/N_{\rm CN}$ 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 $N_{\rm CCN}$ by integrating the product of the measured size-distributed $N_{\rm CN}$ and the aver-

- aged 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).





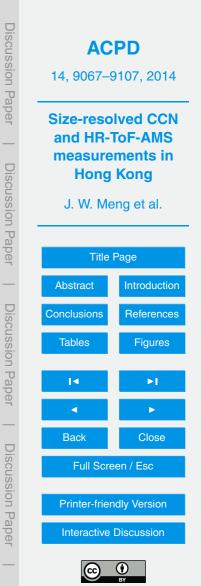
In this study, we report for the first time size-resolved measurements of CCN activity in Hong Kong. We correlated the CCN-derived hygroscopicity ($\kappa_{\rm CCN}$) with those estimated from the size-dependent aerosol chemical compositions determined by an Aerodyne high-resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS,

- ⁵ 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, κ_{AMS}, and some assumed constants. Finally, using the average D₅₀ and the size-resolved CCN activation ratios from the
 10 CCN measurements, we examined the relative importance of hygroscopicity and mix
 - ing state in $N_{\rm CCN}$ 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 Lmin^{-1} after passing through a PM_{2.5} cyclone on the roof of the Supersite (appropriately 20 ma.s.l.) and into a stainless steel

⁵ 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.

0 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_{CN} measurements and the other into the CCNc-200 for N_{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 Lmin^{-1} for the DMA, 0.5 Lmin^{-1} for the WCPC and the CCNc-200 each, and the closed-loop sheath air flow rate was 10 Lmin^{-1} . 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} ($D_{\rm m}$) 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.



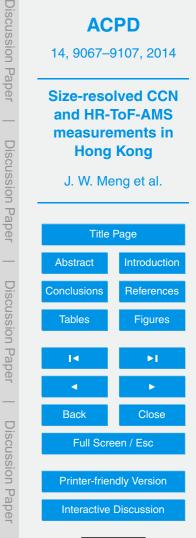


The CCNc-200 was operated at a total flow rate of 1 Lmin^{-1} , of which 0.5 Lmin^{-1} was for column A connected to the DMA to measure the size-resolved CCN spectrum and another 0.5 Lmin⁻¹ was for column B connected to the sample inlet system to measure the total $N_{\rm CCN}$. A sheath-to-aerosol flow ratio of 10 was used. Lathem and Nenes (2011) pointed out that the direct measurements could lead to underestima-5 tions of bulk $N_{\rm CCN}$ 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_{CCN} integrated from size-resolved CCN measurement using column A are usually fewer than $5000 \,\mathrm{cm}^{-3}$ and they correlate well with that from the direct measurement using column B with a slope of 0.97 and correlation coefficient 10 (R^2) of 0.53 as shown in Fig. S1. We use bulk N_{CCN} calculated from column A for the comparison with N_{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 15

unreliable spectra if they occur during a voltage up-scan (Moore et al., 2010). In our measurements, the instrument profiles were allowed up to $\sim 2 \text{ min}$ to stabilize whenever the temperature gradient was changed. At SS = 0.15%, a longer time ($\sim 4 \text{ min}$) 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).

25





2.2.3 Aerosol chemical compositions

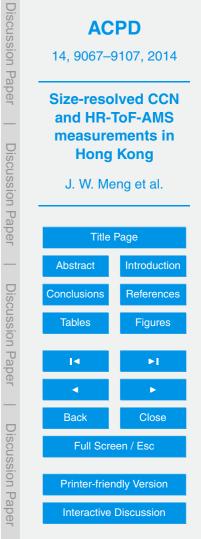
Non-refractory PM_1 (NR- PM_1) constituents of sulfate, nitrate, ammonium, chloride, and organics were measured with the AMS operated under V, pToF, and W modes. The principle behind the instrument has been described in detail elsewhere (DeCarlo et al.,

- ⁵ 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.,
- ¹⁰ 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 be-
- fore 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*_{CN} and *N*_{CCN} distributions were obtained using the TSI Aerosol Instrument Manager (AIM) software (Wang and Flagan, 1989) and CCN acquisition ²⁵ 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 $N_{\rm CCN}$ to $N_{\rm CN}$ 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 Eq. (1) (see Sect. 2.3.3) (Moore et al., 2010; Padró ⁵ et al., 2010).

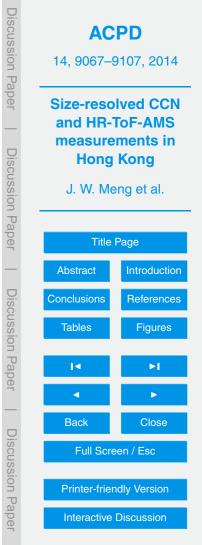
2.3.2 HR-ToF-AMS data

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). 10 The size-resolved mass spectra for vacuum aerodynamic diameter (D_{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 sizeresolved AMS data with those of SMPS and CCNc measurements directly, the AMS $D_{\rm va}$ 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 chemical compositions were calculated from the mass concentrations using densities of organics and inorganics of $1.3 \,\mathrm{g \, cm^{-3}}$ and $1.75 \,\mathrm{g \, cm^{-3}}$, respectively (Alfarra et al., 2006; Cross et al., 2007; Gunthe et al., 2009; King et al., 20 2007; Lee et al., 2013).

2.3.3 D_{50} , $\kappa_{\rm CCN}$ and $\kappa_{\rm AMS}$

25

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:

$$\frac{N_{\rm CCN}}{N_{\rm CN}} = \frac{B}{\left(1 + \frac{D_{\rm p}}{D_{\rm 50}}\right)^c}$$

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 ($\kappa_{\rm CCN}$) is determined from D_{50} by:

10
$$\kappa_{\rm CCN} = \frac{4A^3\sigma_{\rm s/a}^3(T)}{27T^3D_{50}^3\ln^2S_{\rm c}}$$

where $A = 8.69251 \times 10^{-6} \text{ Km}^3 \text{ J}^{-1}$, $\sigma_{\text{s/a}}(T)$ 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 κ_{CCN} in this paper (Petters and Kreidenweis, 2013; Sullivan et al., 2009).

The hygroscopic parameter κ_{AMS} can be obtained from AMS measurements using

$$\kappa_{\rm AMS} = \sum_{i}^{n} f_i \kappa_i \tag{3}$$

where f_i and κ_i are the size-resolved volume fraction derived from AMS measurements and the hygroscopic parameter of the species *i*, respectively (Petters and Kreidenweis, 2007). In this study, the Eq. (3) is simplified as:

$$\kappa_{\text{AMS}} = \kappa_{\text{org}} \times f_{\text{org}} + \kappa_{\text{inorg}} \times f_{\text{inorg}}$$

(1)

(2)

(4)

3 Results and discussion

3.1 Overview

Figure 2 shows an overview of the bulk $N_{\rm CCN}$ concentrations and $N_{\rm CCN}/N_{\rm CN}$ activation ratio at SS of (a) 0.15%, (b) 0.35%, (c) 0.50%, and (d) 0.70%, as well as (e) the bulk $N_{\rm CN}$ 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 1. The gaps in the data in Fig. 2 are due to instrument downtime. For most of the time, the total $N_{\rm CCN}$ at SS of 0.15%, 0.35%, 0.50% and 0.70% were below $800 \,{\rm cm}^{-3}$, $3000 \,{\rm cm}^{-3}$, $5000 \,{\rm cm}^{-3}$ and $5600 \,{\rm cm}^{-3}$ respectively, and $N_{\rm CN}$ was below $10\,000 \,{\rm cm}^{-3}$. Both $N_{\rm CCN}$ and $N_{\rm CN}$ in this study are lower than those observed in July 2006 in Guangzhou (Rose et al., 2010). Large fluctuations in the bulk $N_{\rm CCN}/N_{\rm CN}$ ratios were also observed. The bulk $N_{\rm CCN}/N_{\rm CN}$ 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 $N_{\rm CCN}, N_{\rm CN}$ and $N_{\rm CCN}/N_{\rm CN}$ ratio varied greatly during the campaign.

The bulk mass concentrations of NR-PM₁ ranged from 0.8 μgm⁻³ to 72.4 μgm⁻³ with a mean value of 14.5±9.7 μgm⁻³ as shown in Fig. 2e. The average bulk volume fractions of NR-species were 53±10%, 25±13%, 18±4%, 4±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 (15 May) and the other was a hazy period (28–30 May). During the foggy period, the average RH was 91 % and the bulk NR-PM₁ was as high as $30 \,\mu gm^{-3}$ (Fig. 2e; Li

et al., 2013). The hazy period saw the highest mass concentration of NR-PM₁ species recorded during the whole campaign, but the RH was relatively low (66 %). The highest degree of oxygenation of organic aerosol (OA) with O: C ratio = 0.51 and fraction of



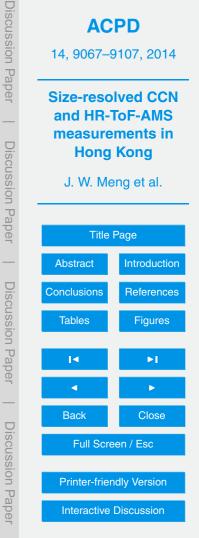
organic at m/z44 = 0.15 occurred during the hazy period due to gas-phase oxidation under high solar irradiance (Li et al., 2013). The average species concentrations of sulfate and organics and the degree of oxygenation of OA oxygenation were lower in the non-foggy/hazy periods (non-episode period) than in the foggy/hazy periods (Li et al., 2013). As shown in Table 2, the mass concentrations of organics, sulfate and nitrate in 5 the hazy period were two to three times higher than those in the rest of the campaign. The mean bulk $N_{\rm CN}$ was 5100 cm⁻³ during the hazy period and 2900 cm⁻³ during the non-episode period. The mean bulk $N_{\rm CCN}$ ranged from 1100 cm⁻³ at SS = 0.15 % to 5300 cm^{-3} at SS = 0.70% during the hazy period, while it ranged from 300 cm^{-3} at SS = 0.15% to 2700 cm^{-3} at SS = 0.70% during non-episode periods.

3.2 f. $\kappa_{\rm CCN}$ and $\kappa_{\rm AMS}$

10

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) 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 2. 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 20 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).

Figure 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



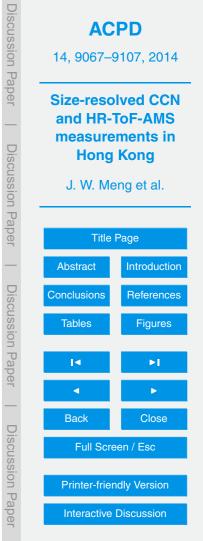


ranged from 0.73 at 42 nm to 0.25 at 200 nm. Additionally, the bulk volume ratio of organics to inorganics between 42 nm and 200 nm was 0.65 in the foggy period, 1.33 in the hazy period, and 0.87 in the non-episode periods.

- The measured κ_{CCN} (yellow symbols) and the calculated κ_{AMS} (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 κ_{CCN} and κ_{AMS} 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 κ_{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 κ_{CCN} was most obvious at SS = 0.15%, at which D_{50} was around 110 nm, and the correspond-
- ing 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 κ_{AMS} calculated from Eq. (3) assuming $\kappa_{org} = 0.1$ and $\kappa_{inorg} = 0.6$ agreed well with the measured κ_{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 ²⁰ better agreement between κ_{AMS} and κ_{CCN} , which can be explained by a high degree of oxygenation of aerosols with O : C ratio up to 0.51 for the organics species observed (Li et al., 2013), leading to a high hygroscopicity (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 $\kappa_{\rm CCN}$ and the sizeresolved organic volume fraction ($f_{\rm org}$) 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 µgm⁻³ were used. Extrapolation of the least square fit line in Fig. 4a and b to $f_{\rm org} = 1$ yields $\kappa_{\rm org} = 0.21 \pm 0.02$ and 0.09 ± 0.01 for the





organic fraction and extrapolation to $f_{\rm org} = 0$ yields $\kappa_{\rm inorg} = 0.59 \pm 0.03$ and 0.59 ± 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 $\kappa_{\rm org} = 0.1$ and $\kappa_{\rm inorg} = 0.6-0.7$ in earlier studies

- ⁵ 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). κ_{AMS} correlates reasonably well with κ_{CCN} , with R^2 of 0.51, as shown in Fig. S2.
- ¹⁰ On the other hand, the mean value of κ_{AMS} 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 κ_{CCN} ranging from 0.39 to 0.28 for SS of 0.15 % to 0.7 % as shown in Table 4. Size-resolved AMS measurements are needed to accurately determine the hygroscopicity parameter and predict N_{CCN} (Cubison et al., 2008; Moore et al., 2012a).
- ¹⁵ 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 $N_{\rm CCN}$ prediction were carried out based on the measured sizeresolved $N_{\rm CN}$ distributions and the AMS measurements. In the first approach, we assumed internal mixing and used $\kappa_{\rm AMS}$ from (i) bulk and (ii) the size-resolved AMS mea-²⁰ surements for each dataset in Eq. (4), and (iii) assumed constant κ values. The corresponding individual D_{50} was then calculated from these κ estimates using Eq. (2), based on which $N_{\rm CCN}$ was predicted. Furthermore, we also used the average D_{50} over the whole campaign in $N_{\rm CCN}$ prediction. Table 3 summarizes the assumptions and parameters used in these methods. In these cases $N_{\rm CCN}$ was calculated by integrating the measured size-resolved $N_{\rm CN}$ 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 $N_{\rm CCN}$ predictions at different SS by comparing the $N_{\rm CCN}$ using the





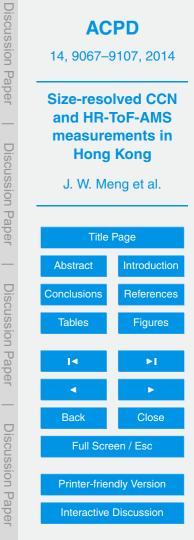
average D_{50} with an internal mixing assumption and the size-resolved CCN activation ratios from CCN measurements which reflect the actual mixing state of the aerosols. The last approach involved integrating the product of the measured size-distribution of $N_{\rm CN}$ and the size-resolved CCN activation ratio in each particle size bin.

5 3.3.1 Prediction of $N_{\rm CCN}$ based on $\kappa_{\rm AMS}$

κ_{AMS} from bulk AMS measurements

The hygroscopicity κ_{AMS} was estimated by assuming that all particles have the same chemical composition as determined by bulk AMS measurements and $\kappa_{\rm org}$ = 0.1 and $\kappa_{\text{inorg}} = 0.6$. The closure results are shown in Fig. 5 and Table 4. Overall, the approaches of using individual D_{50} and the average D_{50} grossly over-predicted $N_{\rm CCN}$ 10 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 15 volume fraction as shown in Table 2 and Fig. 3. Therefore, deriving κ_{AMS} from bulk AMS measurements leads to a positive bias toward inorganic species, and hence an overestimation of κ_{AMS} and N_{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 20

as SS decreases, except for data at SS = 0.15 %, where the $N_{\rm CCN}$ 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.



κ_{AMS} from size-resolved AMS measurements

Figure 6a–d and e–h show the correlations between the measured N_{CCN} and the N_{CCN} predicted from the individual D_{50} of each data set and the averaged D_{50} derived from size-resolved κ_{AMS} , respectively. The slope and R^2 are given in Table 4. In general, the

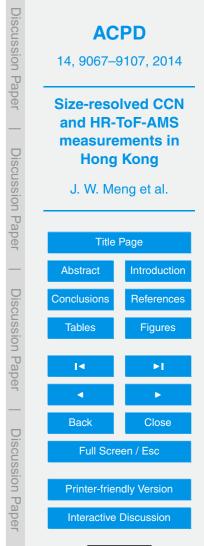
⁵ $N_{\rm CCN}$ prediction deviated by 10% or less for both approaches and the average D_{50} adequately reflects the aerosol activation properties. At SS = 0.70%, individual D_{50} and the average D_{50} gave the close deviations of 10% and 9% respectively between the measured and predicted $N_{\rm CCN}$. At high SS, where even particles of moderate hygroscopicity are activated (Kim et al., 2011), the $N_{\rm CCN}$ 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 $N_{\rm CCN}$ 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% $(D_{50} = 67 \text{ nm})$,

¹⁵ 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 $N_{\rm CCN}$ 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 $N_{\rm CCN}$ (Rose et al., 2011; Wang et al., 2010). When SS decreased, D_{50} increased and the impact of HOA on the $N_{\rm CCN}$ predictions decreased because of their smaller abundance relative to the hygroscopic inorganics. The large deviation in $N_{\rm CCN}$ prediction at SS = 0.15 % may be due to the uncertainty in the low number counts of CCN measurements or the high sensitivity of $N_{\rm CCN}$ to hygroscopicity at low SS as discussed later.

25 3.3.2 Prediction of $N_{\rm CCN}$ from the constant κ

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 $N_{\rm CCN}$ 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 size-resolved $\kappa_{\rm AMS}$ over the campaign at

- ⁵ the four SS), and 0.35 to estimate $N_{\rm CCN}$. Overall, using $\kappa = 0.35$ overestimated $N_{\rm CCN}$ 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. S3 and Table 4. 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
- ¹⁰ $N_{\rm CCN}$ prediction for the three κ decreased gradually from 14 % at SS = 0.15 % to 2 % at SS = 0.70 %. These results further confirm that the prediction of $N_{\rm CCN}$ is less sensitive to κ at high SS than at low one, and that the impact of hygroscopicity on the $N_{\rm CCN}$ prediction decreases with increasing SS.
- The difference in the sensitivity of predicted $N_{\rm CCN}$ to hygroscopicity at different SS ¹⁵ 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. 7a) in this campaign. At SS = 0.15 %, D_{50} is approximately 116 nm and on the right of the main mode (Fig. 7b), a slight variation of κ and D_{50} will cause a large change in $N_{\rm CCN}$ prediction. On the contrary, at SS = 0.70 %, the corresponding D_{50} = 46 nm is on the left of the main mode (Fig. 7c), a variation of κ and D_{50} will have less impact on $N_{\rm CCN}$ prediction as the $N_{\rm CCN}$ is dominated by the mode at 70 nm.

In addition, we carried out the $N_{\rm CCN}$ 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) $\kappa_{AMS} = 0.35$ over the hazy period only. As shown in Fig. S4, using $\kappa_{AMS} = 0.33$ 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_{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 $N_{\rm CCN}$ (Table 4) comparable to those using the size-resolved $\kappa_{\rm AMS}$ and better than those using κ from bulk AMS measurement at all four SS.

5 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 $N_{\rm CCN}$. In this section, we first calculate $N_{\rm CCN}$ by integrating the measured size-resolved $N_{\rm CN}$ 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 $N_{\rm CN}$ and the average size-resolved CCN activation ratio in each particle size bin. The size-resolved $N_{\rm CCN}/N_{\rm CN}$ activation ratios reflect the influences of both the size-resolved chemical compositions and mixing state

- ¹⁵ on CCN activity, and thus can potentially be used to examine the relative importance of mixing state and hygroscopicity in closure analysis when 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 infor-
- ²⁰ mation 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. S5. Data points are shown as means ± standard deviations.

The correlations of measured and predicted $N_{\rm CCN}$ based on the average D_{50} (a–d) and the average size-resolved activation ratio (e–h) are shown in Fig. 8. The slopes of the fitted lines and R^2 at different SS are given in Table 4. The predicted and the measured $N_{\rm CCN}$ differed by less than 10% using the average D_{50} . The difference is comparable to those using the average D_{50} from size-resolved $\kappa_{\rm AMS}$ (Fig. 6e–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_{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%

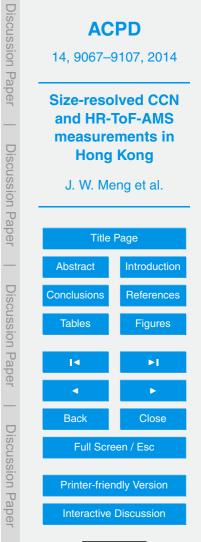
- ⁵ in N_{CCN} (Table 4). From the AMS measurements, the portion of non/less-hygroscopic species inferred by the fractions of f_{43} and f_{57} increased as the particle size decreased (Lee et al., 2013). Because of their higher abundance, their mixing with the hygroscopic components has a higher impact 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 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.

Figure 9 shows the $N_{\rm CCN}$ predicted based on the average D_{50} and the average sizeresolved CCN activation ratio over the hazy period, which was chosen for its higher 15 non/less hygroscopic OA contents and fractions. 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 $N_{\rm CCN}$ prediction more at high SS than at the low SS and that $N_{\rm CCN}$ prediction is more sensitive to mixing state at high SS than hygrocopicity.

4 Conclusions

25

In this study, a DMT CCNc-200 for $N_{\rm CCN}$ measurement, a TSI SMPS for $N_{\rm CN}$ 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 $\kappa_{\rm AMS}$ estimated from bulk and size-resolved AMS measurement assuming internal mixing state. The deviation of $N_{\rm CCN}$ predicted from the individual D_{50} obtained from





 κ_{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. Bulk PM₁ κ_{AMS} grossly over-predicted N_{CCN} by up to 26% because of the positive bias toward the inorganic fraction. On the contrary, the

⁵ N_{CCN} prediction based on size-resolved κ_{AMS} was within 10% of the measurements. An accurate description of κ incorporating size-dependent compositions is necessary for good N_{CCN} predictions.

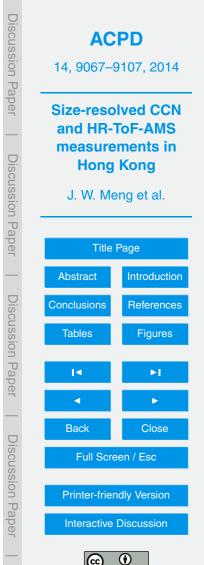
We compared the sensitivity of the $N_{\rm CCN}$ prediction to hygroscopicity (based on assumed internal mixing and κ estimates) and mixing state at different SS. $N_{\rm CCN}$ was found to be more sensitive to hygroscopicity than to mixing state at SS = 0.15 % but the reverse is true at SS = 0.70 %. At SS = 0.15 %, D_{50} (116 nm) is larger than the mode diameter of the typical aerosol distributions we observed. A slight variation in κ (and D_{50}) would have a larger effect on $N_{\rm CCN}$ 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 per-

¹⁵ 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 $N_{\rm CCN}$ prediction at this high SS.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/9067/2014/ acpd-14-9067-2014-supplement.pdf.

20

Acknowledgements. This work was supported by the University Grants Committee (Special Equipment Grant, SEG-HKUST07), Research Grants Council (GRF 600413) and the Environmental Conservation Funds (ECF) of Hong Kong (project no. ECWW09EG04).



References

5

10

- Alfarra, M. R., Paulsen, D., Gysel, M., Garforth, A. A., Dommen, J., Prévôt, A. S. H., Worsnop, D. R., Baltensperger, U., and Coe, H.: A mass spectrometric study of secondary organic aerosols formed from the photooxidation of anthropogenic and biogenic precursors in a reaction chamber, Atmos. Chem. Phys., 6, 5279-5293, doi:10.5194/acp-6-5279-2006, 2006.
- 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.
- Asa-Awuku, A., Nenes, A., Gao, S., Flagan, R. C., and Seinfeld, J. H.: Water-soluble SOA from Alkene ozonolysis: composition and droplet activation kinetics inferences from analysis of
- CCN activity, Atmos. Chem. Phys., 10, 1585–1597, doi:10.5194/acp-10-1585-2010, 2010. Asa-Awuku, A., Moore, R. H., Nenes, A., Bahreini, R., Holloway, J. S., Brock, C. A., Middlebrook, A. M., Ryerson, T. B., Jimenez, J. L., and DeCarlo, P. F.: Airborne cloud condensation nuclei measurements during the 2006 Texas Air Quality Study, J. Geophys. Res.-Atmos., 116. D11201. doi:10.1029/2010id014874. 2011. 15
- 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.
- Chan, C. K. and Yao, X.: Air pollution in mega cities in China, Atmos. Environ., 42, 1–42, 2008. 20 Chang, R. Y.-W., Slowik, J. G., Shantz, N. C., Vlasenko, A., Liggio, J., Sjostedt, S. J., Leaitch, W. R., and Abbatt, J. P. D.: The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: relationship to degree of aerosol oxidation, Atmos. Chem. Phys., 10, 5047–5064, doi:10.5194/acp-10-5047-2010, 2010.
- 25
- Cheng, Y. F., Eichler, H., Wiedensohler, A., Heintzenberg, J., Zhang, Y. H., Hu, M., Herrmann, H., Zeng, L. M., Liu, S., and Gnauk, T.: Mixing state of elemental carbon and non-light-absorbing aerosol components derived from in situ particle optical properties at Xinken in Pearl River Delta of China, J. Geophys. Res.-Atmos., 111, D20204, doi:10.1029/2005id006929.2006. 30
 - Cross, E. S., Slowik, J. G., Davidovits, P., Allan, J. D., Worsnop, D. R., Jayne, J. T., Lewis[†], D. K., Canagaratna, M., and Onasch, T. B.: Laboratory and ambient particle density determinations





using light scattering in conjunction with aerosol mass spectrometry, Aerosol Sci. Tech., 41, 343–359, 2007.

- Cubison, M. J., Ervens, B., Feingold, G., Docherty, K. S., Ulbrich, I. M., Shields, L., Prather, K., Hering, S., and Jimenez, J. L.: The influence of chemical composition and mixing state of
- ⁵ Los Angeles urban aerosol on CCN number and cloud properties, Atmos. Chem. Phys., 8, 5649–5667, doi:10.5194/acp-8-5649-2008, 2008.
 - DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, Aerosol Sci. Tech., 38, 1185–1205, 2004.
- ¹⁰ DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal. Chem., 78, 8281–8289, 2006.

Deng, Z. Z., Zhao, C. S., Ma, N., Liu, P. F., Ran, L., Xu, W. Y., Chen, J., Liang, Z., Liang, S.,

¹⁵ Huang, M. Y., Ma, X. C., Zhang, Q., Quan, J. N., Yan, P., Henning, S., Mildenberger, K., Sommerhage, E., Schäfer, M., Stratmann, F., and Wiedensohler, A.: Size-resolved and bulk activation properties of aerosols in the North China Plain, Atmos. Chem. Phys., 11, 3835– 3846, doi:10.5194/acp-11-3835-2011, 2011.

Deng, Z. Z., Zhao, C. S., Ma, N., Ran, L., Zhou, G. Q., Lu, D. R., and Zhou, X. J.: An examination

- of parameterizations for the CCN number concentration based on in situ measurements of aerosol activation properties in the North China Plain, Atmos. Chem. Phys., 13, 6227–6237, doi:10.5194/acp-13-6227-2013, 2013.
 - Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F., Hings, S., Jung, D., Borrmann. S., and Andreae, M. O.: Size matters more
- than chemistry for cloud-nucleating ability of aerosol particles, Science, 312, 1375–1378, 2006.
 - Ervens, B., Cubison, M., 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
- ³⁰ due to humidity, J. Geophys. Res., 112, D10S32, doi:10.1029/2006JD007426, 2007. Ervens, B., Cubison, M. J., Andrews, E., Feingold, G., Ogren, J. A., Jimenez, J. L., Quinn, P. K., Bates, T. S., Wang, J., Zhang, Q., Coe, H., Flynn, M., and Allan, J. D.: CCN predictions using simplified assumptions of organic aerosol composition and mixing state: a synthesis from





six different locations, Atmos. Chem. Phys., 10, 4795–4807, doi:10.5194/acp-10-4795-2010, 2010.

Gong, Z., Lan, Z., Xue, L., Zeng, L., He, L., and Huang, X.: Characterization of submicron aerosols in the urban outflow of the central Pearl River Delta region of China, Front. Environ.

⁵ Sci. Eng., 6, 725–733, 2012.

10

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.

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.

- Hersey, S. P., Craven, J. S., Schilling, K. A., Metcalf, A. R., Sorooshian, A., Chan, M. N., Flagan, R. C., and Seinfeld, J. H.: The Pasadena Aerosol Characterization Observatory (PACO): chemical and physical analysis of the Western Los Angeles basin aerosol, Atmos. Chem. Phys., 11, 7417–7443, doi:10.5194/acp-11-7417-2011, 2011.
- ²⁰ Huang, X. H., Bian, Q., Ng, W. M., Louie, P. K., and Yu, J. Z.: Characterization of PM_{2.5} major components and source investigation in suburban Hong Kong: a one year monitoring study, Aerosol Air Qual. Res., 14, 237–250, 2014.
 - Kammermann, L., Gysel, M., Weingartner, E., Herich, H., Cziczo, D. J., Holst, T., Svenningsson, B., Arneth, A., and Baltensperger, U.: Subarctic atmospheric aerosol composition: 3.
- measured and modeled properties of cloud condensation nuclei, J. Geophys. Res., 115, D04202, doi:10.1029/2009JD012447, 2010.
 - Kerminen, V.-M., Paramonov, M., Anttila, T., Riipinen, I., Fountoukis, C., Korhonen, H., Asmi, E., Laakso, L., Lihavainen, H., Swietlicki, E., Svenningsson, B., Asmi, A., Pandis, S. N., Kulmala, M., and Petäjä, T.: Cloud condensation nuclei production associated with atmospheric
- nucleation: a synthesis based on existing literature and new results, Atmos. Chem. Phys., 12, 12037–12059, doi:10.5194/acp-12-12037-2012, 2012.
 - 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 mea-





sured at two remote islands of Korea between 2006 and 2009, Atmos. Chem. Phys., 11, 12627–12645, doi:10.5194/acp-11-12627-2011, 2011.

- King, S. M., Rosenoern, T., Shilling, J. E., Chen, Q., and Martin, S. T.: Cloud condensation nucleus activity of secondary organic aerosol particles mixed with sulfate, Geophys. Res.
- 5 Lett., 34, L24806, doi:10.1029/2007GL030390, 2007.
- Lambe, A. T., Onasch, T. B., Massoli, P., Croasdale, D. R., Wright, J. P., Ahern, A. T., Williams, L. R., Worsnop, D. R., Brune, W. H., and Davidovits, P.: Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA), Atmos. Chem. Phys., 11, 8913–8928, doi:10.5194/acp-11-8913-2011, 2011.
 - Lance, S., Nenes, A., Medina, J., and Smith, J. N.: Mapping the operation of the DMT continu-
 - ous flow CCN counter, Aerosol Sci. Tech., 40, 242–254, 2006. Lance, S., Nenes, A., Mazzoleni, C., Dubey, M. K., Gates, H., Varutbangkul, V., Rissman, T. A.,
 - Murphy, S. M., Sorooshian, A., and Flagan, R. C.: Cloud condensation nuclei activity, closure, and droplet growth kinetics of Houston aerosol during the Gulf of Mexico Atmo-
- sure, and droplet growth kinetics of Houston aerosol during the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), J. Geophys. Res., 114, D00F15, doi:10.1029/2008JD011699, 2009.
 - Lathem, T. L. and Nenes, A.: Water vapor depletion in the DMT continuous-flow CCN chamber: Effects on supersaturation and droplet growth, Aerosol Sci. Tech., 45, 604–615, 2011.
- Lathem, T. L., Beyersdorf, A. J., Thornhill, K. L., Winstead, E. L., Cubison, M. J., Hecobian, A., Jimenez, J. L., Weber, R. J., Anderson, B. E., and Nenes, A.: Analysis of CCN activity of Arctic aerosol and Canadian biomass burning during summer 2008, Atmos. Chem. Phys., 13, 2735–2756, doi:10.5194/acp-13-2735-2013, 2013.
 - Lee, B. P., Li, Y. J., Yu, J. Z., Louie, P. K., and Chan, C. K.: Physical and chemical characterization of ambient aerosol by HR-ToF-AMS at a suburban site in Hong Kong during springtime 2011, J. Geophys. Res.-Atmos., 118, 8625–8639, doi:10.1002/jgrd.50658, 2013.
 - Li, Y. J., Lee, B. Y. L., Yu, J. Z., Ng, N. L., and Chan, C. K.: Evaluating the degree of oxygenation of organic aerosol during foggy and hazy days in Hong Kong using high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS), Atmos. Chem. Phys., 13, 8739–8753,
- ³⁰ doi:10.5194/acp-13-8739-2013, 2013.

25

Low, R. D. H.: A generalized equation for the solution effect in droplet growth, J. Atmos. Sci., 26, 608–611, 1969.





Massoli, P., Lambe, A. T., Ahern, A. T., Williams, L. R., Ehn, M., Mikkila, J., Canagaratna, M. R., Brune, W. H., Onasch, T. B., Jayne, J. T., Petaja, T., Kulmala, M., Laaksonen, A., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles, Geophys. Res. Lett., 37, L24801, doi:10.1029/2010gl045258, 2010.

- Geophys. Res. Lett., 37, L24801, doi:10.1029/2010gl045258, 2010.
 Medina, J., Nenes, A., Sotiropoulou, R. E. P., Cottrell, L. D., Ziemba, L. D., Beckman, P. J., and Griffin, R. J.: Cloud condensation nuclei closure during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign: effects of size-resolved composition, J. Geophys. Res., 112, D10s31, doi:10.1029/2006jd007588, 2007.
- Mei, F., Setyan, A., Zhang, Q., and Wang, J.: CCN activity of organic aerosols observed downwind of urban emissions during CARES, Atmos. Chem. Phys., 13, 12155–12169, doi:10.5194/acp-13-12155-2013, 2013.

Moore, R. H., Cerully, K., Bahreini, R., Brock, C. A., Middlebrook, A. M., and Nenes, A.: Hygroscopicity and composition of California CCN during summer 2010, J. Geophys. Res.-Atmos.,

15 117, D00v12, doi:10.1029/2011jd017352, 2012a.

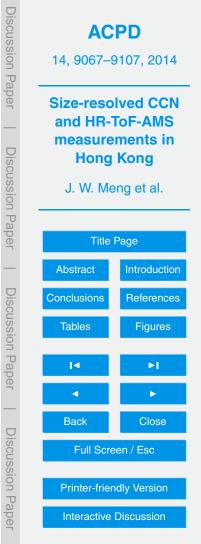
Moore, R. H., Nenes, A., and Medina, J.: Scanning mobility CCN analysis-A method for fast measurements of size-resolved CCN distributions and activation kinetics, Aerosol Sci. Tech., 44, 861–871, 2010.

Moore, R. H., Raatikainen, T., Langridge, J. M., Bahreini, R., Brock, C. A., Holloway, J. S.,

Lack, D. A., Middlebrook, A. M., Perring, A. E., Schwarz, J. P., Spackman, J. R., and Nenes, A.: CCN spectra, hygroscopicity, and droplet activation kinetics of secondary organic aerosol resulting from the 2010 Deepwater Horizon oil spill, Environ. Sci. Technol., 46, 3093–3100, 2012b.

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.
 - Padró, L. T., Tkacik, D., Lathem, T., Hennigan, C. J., Sullivan, A. P., Weber, R. J., Huey, L. G., and Nenes, A.: Investigation of cloud condensation nuclei properties and droplet growth
- kinetics of the water-soluble aerosol fraction in Mexico City, J. Geophys. Res.-Atmos., 115, D09204, doi:10.1029/2009jd013195, 2010.





ConclusionsReferencesTablesFiguresI<</td>▶II<</td>▶II<</td>▶IBackCloseFull Screer / EscPrinter-frierty VersionInteractive DiscussionColspan="2">Colspan="2"Colspan="2">Colspan="2">Colspan="2">Colspan="2"Colspan="2">Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Colspan="2">Colspan="2"Co

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.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth

- and cloud condensation nucleus activity Part 3: Including surfactant partitioning, Atmos. Chem. Phys., 13, 1081–1091, doi:10.5194/acp-13-1081-2013, 2013.
 - 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.
- ¹⁰ Roberts, G. C. and Nenes, A.: A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements, Aerosol Sci. Tech., 39, 206–221, 2005.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Pöschl, U.: Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol

- ¹⁵ particles in theory and experiment, Atmos. Chem. Phys., 8, 1153–1179, doi:10.5194/acp-8-1153-2008, 2008.
 - Rose, D., Nowak, A., Achtert, P., Wiedensohler, A., Hu, M., Shao, 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 1: Size-resolved measurements and implications for
- the modeling of aerosol particle hygroscopicity and CCN activity, Atmos. Chem. Phys., 10, 3365–3383, doi:10.5194/acp-10-3365-2010, 2010.
 - 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 burn-
- ing 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.
 - Stroud, C. A., Nenes, A., Jimenez, J. L., DeCarlo, P. F., Huffman, J. A., Bruintjes, R., Nemitz, E., Delia, A. E., Toohey, D. W., Guenther, A. B., and Nandi, S.: Cloud activating properties of aerosol observed during CELTIC, J. Atmos. Sci., 64, 441–459, 2007.
 - Sueper, D.: ToF-AMS data analysis software: http://cires.colorado.edu/jimenez-group/ ToFAMSResources/ToFSoftware/index.html (last access: 1 June 2012), 2011.

30



14, 9067–9107, 2014

Discussion

Paper

Discussion

Paper

Discussion Pape

Discussion Paper

Size-resolved CCN and HR-ToF-AMS measurements in Hong Kong J. W. Meng et al.

Title Page

Abstract

Introduction

- Sullivan, R. C., Moore, M. J. K., Petters, M. D., Kreidenweis, S. M., Roberts, G. C., and Prather, K. A.: Effect of chemical mixing state on the hygroscopicity and cloud nucleation properties of calcium mineral dust particles, Atmos. Chem. Phys., 9, 3303–3316, doi:10.5194/acp-9-3303-2009, 2009.
- ⁵ Takegawa, N., Miyakawa, T., Watanabe, M., Kondo, Y., Miyazaki, Y., Han, S., Zhao, Y., Van Pinxteren, D., Bruggemann, E., Gnauk, T., Herrmann, H., Xiao, R., Deng, Z., Hu, M., Zhu, T., and Zhang, Y.: Performance of an Aerodyne aerosol mass spectrometer (AMS) during intensive campaigns in China in the summer of 2006, Aerosol Sci. Tech., 43, 189–204, 2009. Tang, I. N. and Munkelwitz, H. R.: Water activities, densities, and refractive indices of aqueous
- ¹⁰ sulfates and sodium nitrate droplets of atmospheric importance, J. Geophys. Res.-Atmos., 99, 18801–18818. doi:10.1029/94id01345. 1994.
 - Textor, C., Schulz, M., Guibert, S., Kinne, S., Balkanski, Y., Bauer, S., Berntsen, T., Berglen, T., Boucher, O., Chin, M., Dentener, F., Diehl, T., Easter, R., Feichter, H., Fillmore, D., Ghan, S., Ginoux, P., Gong, S., Grini, A., Hendricks, J., Horowitz, L., Huang, P., Isaksen, I., Iversen, I.,
- ¹⁵ Kloster, S., Koch, D., Kirkevåg, A., Kristjansson, J. E., Krol, M., Lauer, A., Lamarque, J. F., Liu, X., Montanaro, V., Myhre, G., Penner, J., Pitari, G., Reddy, S., Seland, Ø., Stier, P., Takemura, T., and Tie, X.: Analysis and quantification of the diversities of aerosol life cycles within AeroCom, Atmos. Chem. Phys., 6, 1777–1813, doi:10.5194/acp-6-1777-2006, 2006.
- Wang, J., Cubison, M. J., Aiken, A. C., Jimenez, J. L., and Collins, D. R.: The importance of aerosol mixing state and size-resolved composition on CCN concentration and the variation of the importance with atmospheric aging of aerosols, Atmos. Chem. Phys., 10, 7267–7283, doi:10.5194/acp-10-7267-2010, 2010.
 - Wang, S. C. and Flagan, R. C.: Scanning electrical mobility spectrometer, Aerosol Sci. Tech., 13, 230–240, 1990.
- Wex, H., McFiggans, G., Henning, S., and Stratmann, F.: Influence of the external mixing state of atmospheric aerosol on derived CCN number concentrations, Geophys. Res. Lett., 37, L10805, doi:10.1029/2010gl043337, 2010.
 - Xiao, R., Takegawa, N., Zheng, M., Kondo, Y., Miyazaki, Y., Miyakawa, T., Hu, M., Shao, M., Zeng, L., Gong, Y., Lu, K., Deng, Z., Zhao, Y., and Zhang, Y. H.: Characterization and source
- apportionment of submicron aerosol with aerosol mass spectrometer during the PRIDE-PRD 2006 campaign, Atmos. Chem. Phys., 11, 6911–6929, doi:10.5194/acp-11-6911-2011, 2011.





- Young, K. C. and Warren, A. J.: A reexamination of the derivation of the equilibrium supersaturation curve for soluble particles, J. Atmos. Sci., 49, 1138–1143, 1992.
- Zhang, Z., Engling, G., Lin, C.-Y., Chou, C. C.-K., Lung, S.-C. C., Chang, S.-Y., Fan, S., Chan, C.-Y., and Zhang, Y.-H.: Chemical speciation, transport and contribution of biomass burning smoke to ambient aerosol in Guangzhou, a mega city of China, Atmos. Environ., 44,
- 3187–3195, 2010.

5

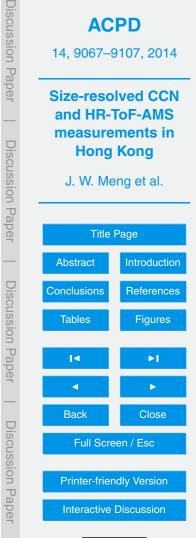
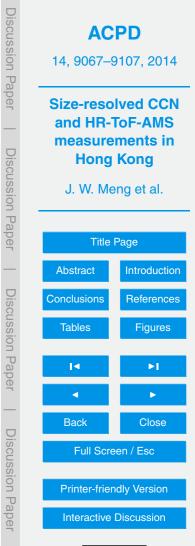




Table 1. Statistics of the bulk N_{CCN} (cm ⁻³) at four SS (%) showing the minimum, maximum,
mean number concentration, the $N_{\rm CCN}/N_{\rm CN}$ ratio, and standard deviation (SD). The last column
shows the number of samples (n) in this campaign.

SS (%)	Max		Mir	-	Mean	n	
	$N_{\rm CCN}~({\rm cm}^{-3})$	$N_{\rm CCN}/N_{\rm CN}$	$N_{\rm CCN}~({\rm cm}^{-3})$	$N_{\rm CCN}/N_{\rm CN}$	$N_{\rm CCN}~({\rm cm}^{-3})$	$N_{\rm CCN}/N_{\rm CN}$	
0.15	2815	0.54	33	0.03	512 ± 452	0.16 ± 0.08	319
0.35	8055	0.78	186	0.08	1546 ± 1137	0.48 ± 0.14	316
0.50	9156	0.82	210	0.12	1815 ± 1285	0.57 ± 0.14	326
0.70	9268	0.92	280	0.16	2082 ± 1484	0.65 ± 0.14	320



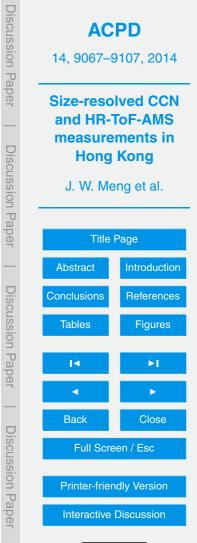


Discussion Paper		PD 9107, 2014
per Discussion Paper	and HR- measure Hong	olved CCN ToF-AMS ements in Kong eng et al.
1 Paper	Title	Page
—	Abstract	Introduction
Disc	Conclusions	References
Discussion Paper	Tables	Figures
Pap	I.◄	▶1
D_		
_	Back	Close
Discussion Pape	Full Scr	een / Esc
on P	Printer-frie	ndly Version
aper	Interactive	Discussion

Table 2. The average size-resolved mass concentrations (μ gm⁻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.

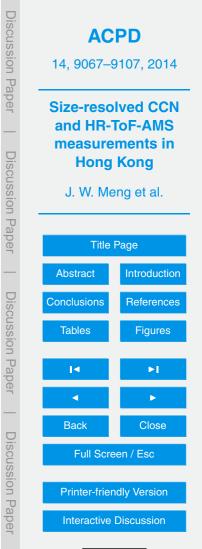
Period	Orga	anics	Sul	fate	Ammo	onium	Nitr	rate	Chl	oride
	Conc.	f								
Foggy	1.60±1.10	0.39 ± 0.12	4.86±3.51	0.45 ± 0.10	1.33±0.98	0.14 ± 0.04	0.18±0.12	0.03 ± 0.00	0.03 ± 0.02	0.001±0.00
Hazy	4.25 ± 2.52	0.57 ± 0.08	5.96 ± 4.36	0.29 ± 0.06	1.71 ± 1.22	0.08 ± 0.03	0.51 ± 0.27	0.06 ± 0.01	0.02 ± 0.01	0.002 ± 0.00
The rest	1.19±0.71	0.47 ± 0.11	2.65 ± 1.86	0.37 ± 0.08	0.81 ± 0.55	0.12 ± 0.03	0.25 ± 0.15	0.04 ± 0.00	0.02 ± 0.01	0.002 ± 0.00

Methods	Mixing state	Chemical composition	K _{AMS}	D ₅₀
I	Internal	Bulk AMS measurements	$\kappa_{AMS} = 0.1 \times f_{org}$ +0.6 × f_{inorg}	Individual
II	Internal	Bulk AMS measurements	$\kappa_{\text{AMS}} = 0.1 \times f_{\text{org}} + 0.6 \times f_{\text{inorg}}$	Average
III	Internal	Size-resolved AMS measurements	$\kappa_{\text{AMS}} = 0.1 \times f_{\text{org}} + 0.6 \times f_{\text{inorg}}$	Individual
IV	Internal	Size-resolved AMS measurements	$\kappa_{\text{AMS}} = 0.1 \times f_{\text{org}} + 0.6 \times f_{\text{inorg}}$	Average
V	Internal	N/A	0.35/0.33/0.30	Constants





Categories	Principles	SS (%)	К	Slope	R
CCN _C	The average D_{50}	0.15	0.39 ± 0.06	1.10	0.9
Ũ	from CCN	0.35	0.36 ± 0.09	1.01	0.9
	measurement	0.50	0.31 ± 0.10	1.05	0.9
		0.70	0.28 ± 0.09	1.08	0.9
	The average CCN	0.15	_	1.09	0.9
	activation ratio	0.35	-	0.99	0.9
		0.50	-	1.02	0.9
		0.70	-	1.04	0.9
AMS	The D_{50} from	0.15	-	1.21	0.9
	bulk K _{AMS}	0.35	-	1.06	0.9
		0.50	-	1.13	0.9
		0.70	-	1.17	0.9
	The average D_{50}	0.15	0.45 ± 0.07	1.26	0.9
	from bulk κ_{AMS}	0.35	0.46 ± 0.06	1.08	0.9
		0.50	0.46 ± 0.06	1.13	0.9
		0.70	0.46 ± 0.07	1.18	0.9
	The D_{50} from	0.15	-	1.06	0.9
	size-resolved	0.35	-	0.94	0.9
	K _{AMS}	0.50	-	1.03	0.9
		0.70		1.10	0.9
	The average D_{50}	0.15	0.37 ± 0.07	1.08	0.9
	from size-resolved	0.35	0.35 ± 0.08	1.01	0.9
	K _{AMS}	0.50	0.31 ± 0.07	1.05	0.9
		0.70	0.29 ± 0.09	1.09	0.9
Others	Constant <i>k</i>	0.15	0.35/0.33/0.30	1.05/0.98/0.91	0.95/0.95/0.9
		0.35	0.35/0.33/0.30	1.01/0.96/0.91	0.95/0.95/0.9
		0.50	0.35/0.33/0.30	1.08/1.05/1.03	0.97/0.97/0.9
		0.70	0.35/0.33/0.30	1.13/1.12/1.11	0.98/0.98/0.9





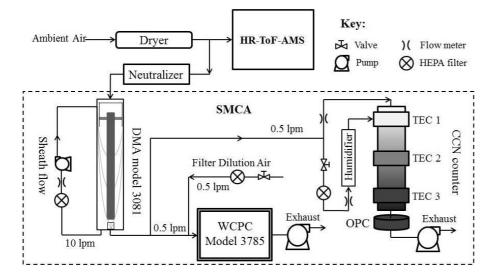
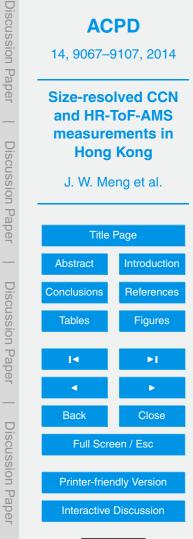
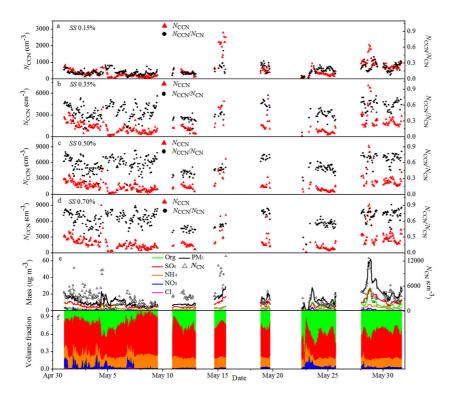
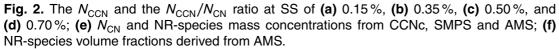


Fig. 1. Schematic of the experimental setup for size-resolved CCN activation and chemical composition measurement.



Discussion Paper







ISCUSSION

Paper

Discussion Paper



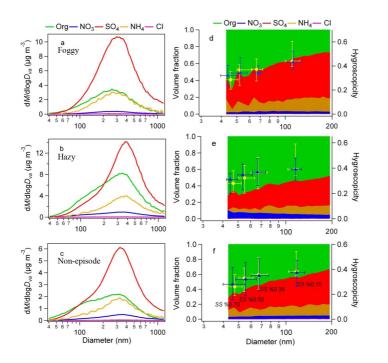
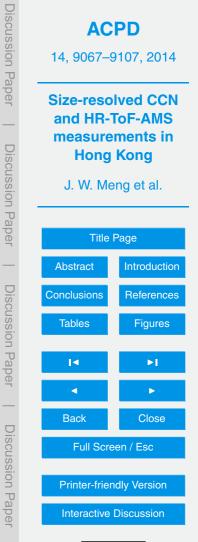
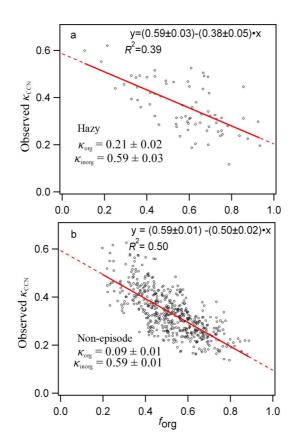
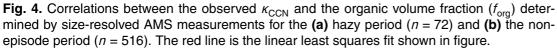


Fig. 3. Size-resolved mass concentration distributions of aerosol chemical composition derived from AMS averaged over (a) the foggy period, (b) the hazy period, and (c) the non-episode periods; the corresponding size-resolved volume fractions of aerosol chemical compositions (colored areas), the observed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



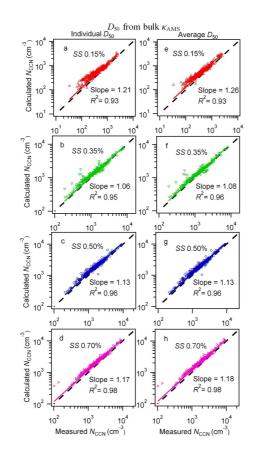


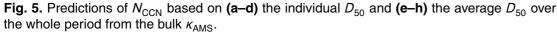


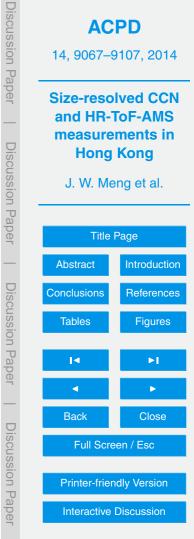












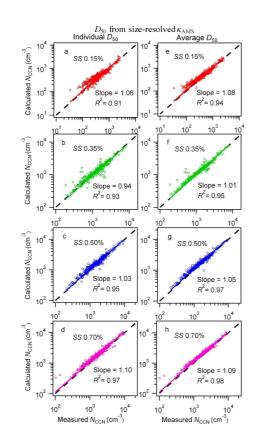
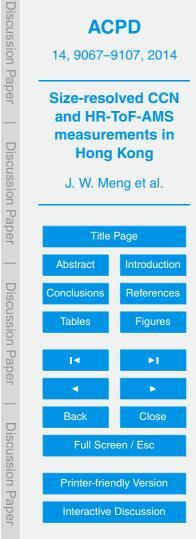


Fig. 6. Predictions of N_{CCN} based on **(a–d)** the individual D_{50} and **(e–h)** the average D_{50} over the whole period from the size-resolved κ_{AMS} .





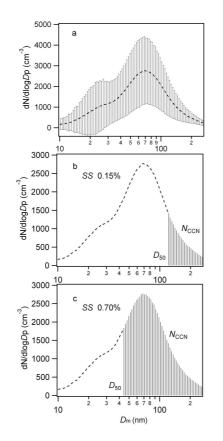


Fig. 7. The average aerosol size distribution over the whole period (a), N_{CCN} prediction based on D_{50} at SS of (b) 0.15% and (c) 0.70%. Data points are mean values and standard deviation.





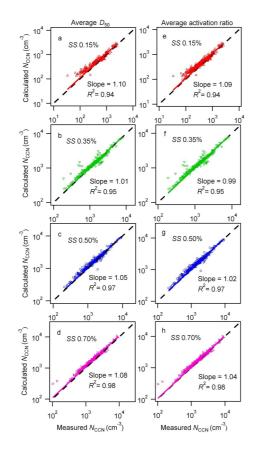


Fig. 8. N_{CCN} estimation in the whole period based on (**a**–**d**) the average D_{50} and (**e**–**h**) the average size-resolved CCN activation ratio from CCN measurement over the whole period.





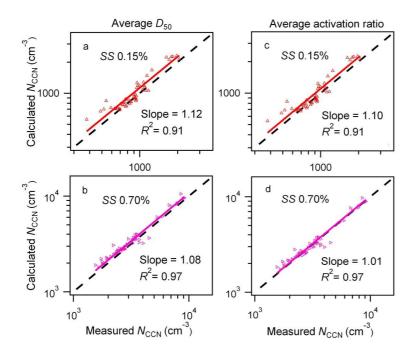


Fig. 9. N_{CCN} estimation in hazy period based on (**a** and **b**) the average D_{50} and (**c** and **d**) the average size-resolved CCN activation ratio from CCN measurement over the hazy period.

