Title
Relationship between hygroscopicity and cloud condensation nuclei activity for urban aerosols in Tokyo

Author(s)
Mochida, Michihiro; Kuwata, Mikinori; Miyakawa, Takuma; Takegawa, Nobuyuki; Kawamura, Kimitaka; Kondo, Yutaka

Citation
Journal of Geophysical Research, 111, D23204
https://doi.org/10.1029/2005JD006980

Issue Date
2006-12-07

Doc URL
http://hdl.handle.net/2115/26163

Rights
An edited version of this paper was published by AGU. Copyright 2006, American Geophysical Union, JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES, 111.

Type
article (author version)

File Information
JGRA111-23204.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP
Relationship between hygroscopicity and cloud condensation nuclei activity for urban aerosols in Tokyo

Michihiro Mochida1*, Mikinori Kuwata2, Takuma Miyakawa2, Nobuyuki Takegawa2, Kimitaka Kawamura1 and Yutaka Kondo2

1 Institute of Low Temperature Science, Hokkaido University, N17, W8, Kita-ku, Sapporo 060-0819, Japan
2 Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

*Corresponding author (e-mail: mochida@pop.lowtem.hokudai.ac.jp)

Submitted to Journal of Geophysical Research - Atmospheres
Abstract: As described by the Köhler theory, the hygroscopicity of atmospheric aerosol particles is a key factor regulating their cloud condensation nuclei (CCN) activity. In this study, the relationship between hygroscopicity and CCN activity for urban aerosol particles was investigated using a hygroscopicity tandem differential mobility analyzer (HTDMA) coupled in series to a CCN counter. The HTDMA-CCNC system was operated near the center of the Tokyo metropolitan area from November 10 to 17, 2004. For aerosol particles whose dry mobility diameters were 30-200 nm, the ratios of CCN to condensation nuclei (CN) at 0.22 -1.3% supersaturation were obtained as a function of particle hygroscopicity at 83 and 89% RH. More-hygroscopic particles were clearly more CCN active than less-hygroscopic particles of the same size, indicating that hygroscopicity is a critical factor regulating CCN activity. The chemical compositions of particles were measured using an aerosol mass spectrometer, and were found to relate closely to CCN activity as well as to the hygroscopicity. The measured CCN–hygroscopicity relationships were compared to those predicted by Köhler theory. The results suggest that CCN activity is possibly perturbed by changes in surface tension due to organics, dissolution/dissociation of water-soluble organics under supersaturation conditions, or different non-ideality of organics from inorganic salts. These factors associated with organics are potentially important for CCN numbers and thus for cloud processes in the atmosphere.
1. Introduction

The effect on climate of anthropogenic sources is one of the major concerns in current global environmental issues. In particular, indirect forcing of atmospheric aerosols via the formation of cloud droplets is an important scientific problem because it currently leads to large uncertainty in the prediction of the radiative forcing and of its perturbation by human activity. Chemical compositions of aerosol particles released from natural and anthropogenic sources are not homogeneous either locally or globally, hence characteristics such as hygroscopicity and surface tension are significantly different from one particle to another, controlling the particle's ability to form cloud droplets. In particular, organic components in particles contribute significantly to CCN concentrations under various conditions [Novakov and Penner, 1993; Matsumoto et al., 1997], and their complex characteristics make the prediction of cloud droplet formation a challenging research subject.

Recently, a number of model studies dealing with the role of organics in cloud formation have been presented [e.g., Chuang et al., 1997; Feingold and Chuang, 2002; Nenes et al., 2002; O’Dowd et al., 2004; Lance et al., 2004; Abdul-Razzak and Ghan, 2004]. Theoretically, cloud droplet formation is enhanced by the dissolution of water-soluble organics and the reduction in surface tension by surface-active materials. By contrast, organic films may deplete droplet formation by retarding the transfer of water from gas phase to particles [Feingold and Chuang, 2002]. A sensitivity study for the prediction of cloud droplet numbers dealing with the above factors suggests that uncertainty in the chemical compositions of aerosol particles strongly contributes to the variability of cloud droplet numbers [Lance et al., 2004]. The importance of reduction of surface tension is in particular discussed in several studies [Nenes et al., 2002; Lance et al., 2004]. However, attempts to measure the surface tension of real particles in the atmosphere are limited [Facchini et al., 1999; 2000], and insufficient to estimate the surface tension of atmospheric aerosol particles
under various conditions. Further, a lack of information on the bulk hygroscopicity (i.e., solute effect) of organics also limits our prediction of cloud droplet formation. Only one constant value of hygroscopicity has been applied in global models dealing with direct and/or indirect effects of organic aerosols [Ghan et al., 2001a, 2001b] despite the fact that the hygroscopicity of organics is recognized to vary depending on their sources and ages [Saxena et al., 1995]. Moreover, the role of the partial dissolution of organics in cloud condensation nuclei (CCN) activity is still under debate. Perturbation of CCN activity due to the partial dissolution of organics has been evaluated by model studies [e.g., Schulman et al., 1996], whereas laboratory experiments imply that particles of slightly water-soluble organics can act as effective CCN as if they were completely soluble [Raymond and Pandis, 2003].

All of the issues described above stimulate the investigation of CCN activity from the viewpoint of particle characteristics other than size. For instance, field measurements using a hygroscopicity tandem differential analyzer (HTMDA) draw attention as a means of measuring the hygroscopicity of particles, a key property for CCN activity [Köhler, 1936]. A number of hygroscopicity studies have been conducted in urban and remote sites, inferring its relevance to CCN activity. In some field studies, hygroscopicity and CCN activity have been measured simultaneously for mono- and poly-dispersed aerosol particles using a HTDMA and a CCN counter in parallel [Brechtel and Kreidenweis, 2000a; Zhou et al., 2001; Roberts et al., 2002; Dusek et al. 2003; Rissler et al., 2004]. These studies have suggested that hygroscopicity is a factor regulating the CCN activity of particles.

In this study, the relationship between hygroscopicity and CCN activity for urban aerosol particles over Tokyo was investigated using a novel instrumental setup: a HTDMA coupled in series to a CCN counter. The HTDMA was used to classify particles according to their hygroscopicity under subsaturation RH conditions (83 and 89 %), and the CCN counter measured the number of CCN particles at supersaturation RH (0.22 to 1.3 %) among the
particles classified by their hygroscopicity. This HTDMA-CCNC system enabled us to measure the CCN activity of urban aerosol particles as functions of dry particle size and of their hygroscopicity. As far as we know, this is the first report in which CCN activities have been investigated for atmospheric particles with specific sizes and hygroscopicities. Here we present results from simultaneous measurements of hygroscopicity and CCN activity of atmospheric particles, and discuss new insights concerning the behavior of CCN and thus mechanisms for the formation and growth of cloud droplets.

2. Experimental

2.1 Köhler theory of the relationship between hygroscopicity and CCN activity

The theory of CCN activation of atmospheric aerosol particles was presented by Köhler [1936], where the activation was explained by the thermodynamic balance of two effects: a decrease in water vapor pressure due to the solute (Raoult effect) and an increase in water vapor pressure due to the curvature at the air-liquid interface (Kelvin effect). For single-solute particles, the equilibrium water vapor saturation ratio $S$ for a droplet can be described by:

$$
\ln S = \frac{2A}{d_{wet}} - \frac{Bd_{ve,dry}^3}{d_{wet}^3 - d_{ve,dry}^3} \left( A \equiv \frac{2\sigma M_w}{\rho_w RT}, \ B \equiv \nu \phi \frac{M_w \rho_s}{M_s \rho_w} \right)
$$

where $d_{wet}$ and $d_{ve,dry}$ are the diameter of the droplet and the volume equivalent diameter of the dry (solute) particle, respectively, $\sigma$ is the surface tension, $M_w$ and $M_s$ are the molecular weights of water and solute, respectively, $\rho_w$ and $\rho_s$ are the density of the water and solute, respectively, $\nu$ is the degree of dissociation, and $\phi$ is the osmotic coefficient. The product of $\nu$ and $\phi$ is equivalent to the so-called van’t Hoff factor [Pruppacher and and Klett, 1997]. $R$ and...
are the gas constant and temperature, respectively. This equation can be extended for a multi-component system, by modifying the hygroscopicity $B$ in Equation 1 to be

$$B = \frac{M_w}{\rho_w} \sum_i v_i \phi_i \varepsilon_i m_i \left/ \sum_i m_i / \rho_i \right. (2),$$

where $v_i$, $\phi_i$, $\varepsilon_i$, $m_i$, $M_i$ are the degree of dissociation, the osmotic coefficient, the degree of dissolution, the mass mixing ratio, and the molecular weight of compound $i$, respectively. This equation is based on the additive effect of solutes, including inorganics and organics. Insoluble compounds such as elemental carbon, crustal materials and hydrophobic organics may also be included in Equation 2, by regarding $M_i$ to be infinity. Note that, as expressed above, the term hygroscopicity in this paper denotes bulk hygroscopicity, and does not include the Kelvin effect of aerosol particles.

Assuming that $A$ and $B$ are constants and that $d_{\text{wet}}$ is much larger than $d_{\text{ve, dry}}$, we can obtain the critical water vapor saturation ratio $S_c$, i.e. the minimum saturation ratio $S$ required to form cloud droplets, with $A$, $B$ and $d_{\text{ve, dry}}$ from

$$\ln S_c = \frac{2}{\sqrt{A \left( \frac{2A}{3d_{\text{ve, dry}}} \right)^{3/2}}} \cong s_c$$

where $s_c$ is the critical water vapor supersaturation ($S_c = 1 + s_c$). CCN activity of the particles is therefore high when the hygroscopicity $B$ and dry diameter $d_{\text{ve, dry}}$ are large, and when the surface tension $\sigma$ is low (i.e. $A$ is low). This study aims to determine simultaneously the hygroscopicity and CCN activity of atmospheric aerosol particles, and to assess the relationship based on Equations 1-3.
2.2 Atmospheric Measurement using HTDMA-CCNC System

The experimental setup of the HTDMA-CCNC system is presented in Figure 1. In the HTDMA part, sample atmospheric aerosols (PM1) were dried in tandem diffusion dryers (TSI Model 3062) filled with silica gel and molecular sieve (13X/4A, Spelco). The reading of a RH sensor (Vaisala HMP237, uncertainty: 2% RH, calibrated at 11.3 and 75.3% RH with LiCl and NaCl saturated solutions) at the outlet of the dryers was below 2% during the HTDMA operation. The RH of the dried aerosols was thereby estimated to be < 4% (= 2% + the uncertainty of the sensor). The sample aerosols were then neutralized in an $^{241}$Am bipolar charger, and classified using a differential mobility analyzer (DMA1, TSI Model 3081). The RH of the sample aerosols was then controlled by a supply of water vapor through a Nafion tube, and the resulting size change of aerosol particles was measured by another DMA (DMA2) combined to a condensation nuclei (CN) counter (TSI Model 3022A). The RH of the circulated sheath flow of DMA2 was also controlled by water vapor exchange through a Nafion tube. The residence time of particles between the outlet of the Nafion humidifier and the inlet of DMA2, which allows particles to equilibrate with the humidified air, was about 10 s. Details of the HTDMA used in this study have been given elsewhere [Mochida and Kawamura, 2004]. Being different from the work in Mochida and Kawamura. [2004], fixed RH conditions in DMA2 were achieved as follows. The RH of both the sample and sheath flows entering DMA2 were controlled by changing the mixing ratios of the humidified and dry air flows supplied as sheath flows to the Nafion tubes. The mixing ratio was adjusted automatically by a Proportional-Integral-Derivative (PID) control with the RH as the input. The RH in DMA2 is defined as the weighted average of RH in the sheath and sample airs by their flow rates. The temperature of the sheath (sample) air was 297.6 ± 0.7 (297.8 ± 0.7) K. An extra Nafion dryer was placed at the outlet of DMA2, so that a dehumidified aerosol
(~10% RH) was introduced to CN and CCN counters and a volatility TDMA (VTDMA) system (see Figure 1).

Part of the processed sample aerosol exiting DMA2 was introduced to the CCN counter [Roberts and Nenes, 2005] (Droplet Measurement Technologies, Boulder, CO) at a sample flow rate of 0.05 liter min\(^{-1}\). This CCN counter can establish supersaturation conditions between 0.1 to 2% in a cylindrical continuous-flow thermal-gradient diffusion chamber. The total flow rate in the chamber was 0.5 liter min\(^{-1}\) and the residence time of aerosol particles in Poiseuille flow was ca. 13 s. The CCN number concentration was measured as a function of the resulting size distribution (i.e. the hygroscopic growth factor \(g\), or hygroscopicity \(B\)). The sheath flow rate of the CCN counter was 0.45 liter min\(^{-1}\). The particle free sheath flow was generated from room air by letting the air pass through a HEPA filter. According to Boltzmann equilibrium of particle charging and the transfer function of the DMA columns, the number of aerosol particles decreases by processing through two DMAs in series. However, the resulting number concentrations of particles (typically 1-20 particles cm\(^{-3}\)) were well above the detection limit of the CN and CCN counters with integration times of 3 min. The diameters of initially dry particles ranged from 30 to 200 nm in the experiments. The RH after humidification was set to be 83 and 89 %, depending on the sampling period. Unless otherwise stated, diameter in this paper means an electrical mobility diameter \(d_{\text{mob}}\) classified by a DMA. Note that the mobility diameter of classified particles has a finite size range (geometric standard deviation: 1.04 for 100 nm particles). Further, small but non-negligible fractions of particles have larger diameters (~ \(\times\)1.5 or more) because of multiple electrostatic charges.

An Aerosol Mass Spectrometer (AMS, Aerodyne) was operated in parallel to the HTDMA-CCNC system to obtain the chemical compositions of aerosol particles. Details of the AMS measurements are described in Jayne et al. [2000] and Takegawa et al. [2005]. Mass
concentrations of chemical components integrated over specific ranges of vacuum aerodynamic diameter ($d_{va}$) measured by the AMS were used to represent the chemical compositions of mono-disperse aerosol particles in the HTMDA-CCNC system. Since the ratio of $d_{va}$ to electrical mobility diameter ($d_{mob}$) can vary depending on particle morphology and density [DeCarlo et al., 2004], we present here the mass concentrations at $d_{va}$ ranging from 50 to 200 nm as estimates of the compositions at $d_{mob} = 100$ nm. The chemical compositions of particles with other mobility diameters used in the HTDMA-CCNC study were not estimated, but the general characteristics may be qualitatively similar to that at $d_{mob} = 100$ nm.

As shown in Figure 1, the VTMDA system with a 400 °C heater was connected to the HTDMA in parallel to the CN and CCN counters. This part of the measurement system was used to quantify the amount of non-volatile components (mainly elemental carbon) in the particles. The results from the instrument are presented in a separate paper [Kuwata et al., 2006].

In parallel to the HTDMA-CCNC and the AMS, a Scanning Mobility Particle Sizer (SMPS, TSI Model 3034) was operated separately to measure the size distribution of ambient particles. Two diffusion dryers with silica gel in series (TSI Model 3062) were placed in front of the SMPS. The mobility size distributions of dry particles were obtained every 3 min.

The aerosol measurements using the HTDMA-CCNC system were carried out at the Research Center for Advanced Science and Technology, the University of Tokyo, Tokyo, Japan from November 10 to 17, 2004. The population of the Tokyo metropolitan area is 41 million, and the measurement site is located near the center of the area. Several different types of measurements were performed during the campaign. From November 10 to 12, temporal variation of hygroscopicity and CCN activity of aerosol particles were obtained semi-continuously for particles whose dry diameters were 100 nm. From November 12 to 16,
particles whose dry diameters were 30, 50, 80, 100, 150, and 200 nm were measured periodically. During the period of November 10-16, the hygroscopicities of particles were measured at 83% RH. On November 17, the hygroscopicities for 50 and 100 nm particles were measured at 89% RH. Only a limited number of samples were measured at 89% RH because of the limited period of the investigation.

Particle number distributions as a function of hygroscopicity was measured every hour during the field measurements, with a scanning time of 5 min. In the 55-min interval, we measured CCN activities every 5 min by changing the particle diameters of the humidified particles (hygroscopicity), and supersaturation RH. Four different supersaturation conditions, 0.22, 0.55, 0.82 and 1.3% (determined by Köhler- and Pitzer equations, see explanations in section 2.4), were applied to the CCN activity measurements. Dry particle diameters were also changed periodically, usually after the 1-hour measurement cycle described above.

### 2.3 Calculation of Hygroscopicity from Hygroscopic Growth Factor

The hygroscopic growth factor $g$, which can be measured using the HTDMA, is the ratio of the humidified to dry particle diameters:

\[
g = \frac{d_{ve}(RH)}{d_{ve,dry}} \approx \frac{d_{mob}(RH)}{d_{mob,dry}}
\]

(4)

where $d_{ve,dry}$ and $d_{ve}(RH)$ (or $d_{mob,dry}$ and $d_{mob}(RH)$) are the dry and humidified volume-equivalent (or mobility) diameters of particles in the HTDMA, respectively. This hygroscopic growth factor $g$ is a function of RH, which increases with increasing RH. In this study, $d_{mob,dry}$ is approximated by the mobility diameter of particles under the condition of $<4\%$ RH in DMA1. The second term on the right side of Equation 1 is expressed with water activity $a_w$ by
The hygroscopic growth factor is defined as:

$$B = (1 - g^3) \ln a_w$$

(6)

Under sub-saturated RH conditions in the HTDMA, $a_w$ is nearly equal to the saturation ratio $S$ (or $RH(\%) / 100$) in equilibrium conditions, but slightly different from $S$, due to the surface tension effect (Kelvin effect) of particles. The relationship between $S$ and $a_w$ is given from Equations 1 and 5 by:

$$S(\equiv RH(\%) / 100) = a_w \exp \left( \frac{2A}{d_{ve}(RH)} \right)$$

(7)

From Equations 6 and 7, both $a_w$ and $B$ can be calculated from $RH$ and $g$ that are directly measured by the HTDMA, and from the surface tension $\sigma$ that is assumed appropriately. Since the prediction of $a_w$ is less sensitive to the uncertainty in $\sigma$ than that in RH, application of the surface tension of pure water is a reasonable assumption for the prediction of $B$. An important point is that hygroscopicity $B$ in Equation 6 is the value derived under subsaturation RH conditions, which is not necessarily the same as that in Equations 1-3 under supersaturated conditions. This is because $\nu$, $\phi$, and $\varepsilon$ are not necessarily constant. For instance, in the case of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ particles whose dry diameters are 100 nm,
the hygroscopicity $B$ at 83% RH, 298 K are calculated to be 0.79 and 0.66 times, respectively, smaller than those at the critical supersaturation, 308 K. This is the point to be discussed in the results and discussion section.

2.4 Derivation of the CCN distribution as a function of hygroscopicity

Particle number (CN) distributions as a function of hygroscopic growth factor were obtained by scanning DMA2 and by recording the number of particles exiting from DMA2, with a size resolution of 64 channels/digit. An example of the scan is shown as a white histogram in Figure 2a. Based on this CN distribution as a function of $g$, the distribution of CCN was obtained as follows. CCN numbers were measured at four different hygroscopic growth factors $g$, 1.00, 1.11, 1.24, and 1.38 (shown as solid circles in Figure 2a). The distributions of hygroscopic growth factors of particles entering the CCN counter for four different set points, $k_j(g)$ ($j = 1, 2, 3$ and 4), were estimated from the experimentally derived transfer function of the first and second DMAs (Figure 2b); the mono-disperse size distribution of (NH$_4$)$_2$SO$_4$ particles processed in the HTDMA under dry conditions ($d_{mob,dry} = 30-200$ nm) was measured by using DMA2 and the CN counter as SMPS, and was approximated to be the transfer functions for the atmospheric particles with the same $d_{mob,dry}$. A fixed half-width of the distribution was applied for particles with different $g$. Although the transfer functions of DMA2 for particles that grow by humidification are different from those for dry particles (Cunningham slip correction is not constant), the error of the half-width associated with this simplification was estimated to be at most 4%. As seen in Figure 2b, particles with some width of hygroscopic growth factor are introduced to the CCN counter even if the classification in the HTDMA is fixed. Figure 2b further shows that the combination of each distribution well covers the entire range of the measured hygroscopic growth factor $g$. Weighting functions $w_j(g)$ ($j = 1, 2, 3$ and 4) presented in Figure 2c are
derived from $k_j(g)$ by the equation:

$$w_j(g) = \frac{k_j(g)}{\sum_j k_j(g)} \quad (10),$$

and are presented in Figure 2c. The CCN distributions as a function of hygroscopicity are then calculated based on the equation:

$$\frac{dy_{CCN}(g)}{d \log g} = \frac{dy_{CN}(g)}{d \log g} \sum_j w_j(g) r_j \quad (11)$$

where $r_j$ is the CCN/CN ratio at four set points of hygroscopic growth factors $g$, and $\frac{dy_{CN}(g)}{d \log g}$ and $\frac{y_{CCN}(g)}{d \log g}$ are number concentrations of CN and CCN as a function of $g$, respectively. An example of the calculated CCN distribution as a function of $g$ is presented as the shaded histogram in Figure 2a.

2.5 Uncertainty in the Measurements

There are three different types of uncertainties in the variables used in this study; i.e. random errors (precision), systematic errors (trueness), and widths of diameter and supersaturation with respect to the mean values. They are summarized in Table 1. Random errors and widths of variables in this paper are presented as one standard deviation (1SD). In this study, any fluctuations in variables under fixed conditions were considered as random errors, even though their frequencies were longer than the sampling rates of the variables. Random and systematic errors are discussed and presented separately in this paper, which makes it possible to assess whether small differences in hygroscopicity and CCN activity are statistically significant.
The random errors in CN and CCN counts were statistically determined to be 1-4% and 2-10%, respectively (Table 1). The random error in the CCN to CN ratio is 2-11%. The systematic error in the CCN/CN ratio was estimated to be less than 10%.

The classification of the first and second DMAs is calibrated by measuring the sizes of standard PSL spheres (STADEX, 70±1 nm, CV 6.22%; 123±2 nm, CV 1.54%; 207±6 nm, CV 1.62%) in the SMPS mode. The size selection of two DMAs was further adjusted by classifying dry (NH₄)₂SO₄ particles with one DMA and by measuring the mode diameter with the other. The same procedure was performed between the second DMA and another (third) DMA used for the calibration of the CCN counter (see section 2.2). Mobility diameters based on the PSL calibration of DMA2 are presented in this paper. Precisions of the mobility diameters of particles classified in the first and second DMAs were 1%. The width of \( d_{\text{mob}} \) classified by the DMAs was estimated to be 4% from size distribution measurements of PSL spheres. Errors associated with the assumption of particle morphology (i.e., \( d_{\text{ve}} = d_{\text{mob}} \)) are discussed in the results and discussion section (section 3.4.3).

Supersaturation in the CCN counter was calibrated by measuring the critical activation dry diameters of (NH₄)₂SO₄ particles classified using a DMA. In the calibration procedure, the CCN/CN ratio measured for (NH₄)₂SO₄ particles is ideally a stepwise function of the dry particle diameters, but it actually shows a gradual increase as a function of the dry diameter. This is due to the width of the supersaturation condition inside the CCN counter, and also of the particle size classified by the DMA. If the widths of critical diameters are assumed to be totally from those of supersaturation in the CCN counter, we can obtain the widths of supersaturation to be ±0.02, ±0.03, ±0.06 and ±0.08% for 0.22, 0.55, 0.82 and 1.3 %, respectively. In this paper, we present supersaturation conditions based on the calibration using the (NH₄)₂SO₄ on the assumption of Köhler curves at \( T = 308 \) K, with \( \phi \) calculated from the Pitzer equation [Pitzer and Mayorga, 1973] (hereafter referred to as KP). The droplet
surface tension of (NH₄)₂SO₄ in this calculation is based on the relationship in Hänel [1976].

As presented in Kreidenweis et al. [2005], some available CCN activation models predict a significantly higher critical supersaturation of (NH₄)₂SO₄ than that from KP. In the discussion section, we also apply the empirical model proposed by Kreidenweis et al. [2005] (hereafter referred to as K2005) to assess the potential uncertainty of the supersaturation conditions. This model is chosen for comparison because its prediction of critical supersaturation is highest among the models summarized in Kreidenweis et al. [2005].

Because K2005 is based on a parameterization at 298 K, a correction factor of 0.952 \( \left( \frac{298}{308} \right)^{3/2} \) derived from Equations 1 and 3 was applied to determine \( s_c \) at 308 K. Note that the standard Köhler model with \( \phi = 1 \), by contrast, gives a lower critical supersaturation than KP with the Pitzer equation. However, the discrepancy is smaller than that between KP and K2005.

The systematic error of RH measurement in the HTDMA is \( \leq 2\% \) above 83 % RH, based on the manufacturer’s warrant of the RH sensors (Vaisala, HMP 237). The random errors of RH at the inlet and outlet of DMA2 were determined to be 0.3% and 0.9%, respectively, from the temporal variations of the RH readings. Possible drift of the sensitivity of the RH sensors was assessed by a 4-day continuous measurement of hygroscopic growth factor \( g \) for 100 nm (NH₄)₂SO₄ particles at 83% RH, which was performed after the field measurement. The 1SD value of \( g \) for (NH₄)₂SO₄ was 0.01 (\( n = 1100 \)), which is explained by 0.5% error in RH. This RH error is in the range of the precisions of the RH reading (0.3-0.9%). The possible drift of RH associated with the sensitivity change of the RH sensors is thereby neglected in this study. The systematic error of RH (\( \leq 2\% \)) leads to \( \leq 2\% \) error in hygroscopic growth factor \( g \), for particles whose hygroscopic growth factor is about 1.2 at 80-85% RH [Mochida and Kawamura, 2004].

The hygroscopic growth factor \( g \) of pure (NH₄)₂SO₄ particles at 83% RH in DMA2
were measured (n = 2) during the field investigation. They measured g were within 2% of that predicted in the literature [Tang and Munkelwitz, 1994], which also supports the validity of the RH control in HTDMA. The random error of g is determined to be 1% from the growth factor measurements of 100 nm (NH₄)₂SO₄ particles at 83% RH after the field investigation.

As described in section 2.3, whether or not the hygroscopicity of particles under supersaturation conditions at 308 K (Bₜₜ) reflects those at 83% and 89% RH, 298 K (B₈₃ and B₈₉) is important for the discussion. If major inorganic salts in sample atmospheric aerosols remain as solids after they are humidified in the HTDMA, then this leads to a large difference between B₈₃ (or B₈₉) and Bₜₜ by change of ε in Equation 2. However, we conclude that this is very unlikely under our experimental conditions, based on the following results. First, when pure (NH₄)₂SO₄ particles of 30-200nm were introduced to the HTDMA system at the RH set points of 83 and 89%, the particle growth expected from its deliquescence was always observed for all particle size ranges, indicating that (NH₄)₂SO₄ does deliquesce under our experimental conditions. This result is consistent with another HTDMA study [Hämeri et al., 2000]. Second, since other possible major components of inorganic salts, such as NH₄NO₃, NH₄Cl, H₂SO₄, NH₄HSO₄, (NH₄)₃H(SO₄)₂ have lower bulk deliquescence RH than (NH₄)₂SO₄, these fractions in atmospheric particles should also deliquesce in the HTDMA system. Third, these inorganic salts are mixed with organics in the atmosphere, and laboratory and field studies show evidence that they usually deliquesce at lower RH than pure salts [Dick et al., 2000; Xu et al., 2003].

Other factors that potentially alter B as a function of RH are discussed in the results and discussion section. They include a change in osmotic coefficient φ of inorganic salts, and changes in νφ, and ε of organic compounds.

Note that, although the uncertainty in the measurements was quantified as much as possible, there are several potential biases that have not been fully quantified in this study.
They include possible changes in the particle chemical composition and morphology in the apparatus. When atmospheric particles were introduced to the HTMDA under dry (<4% RH) conditions in DMA2, no significant decrease in $d_{mob}$ was observed. This implies that, at least between DMA1 and DMA2, evaporation/condensation of semi-volatile compounds and the particle morphology change is negligible under the dry condition. However, possible changes in the composition and morphology in other parts of the apparatus and in different RH conditions were not assessed in this study. Possible evaporation of components in the CCNC at increased temperatures (up to 308 K) and possible absorption of water-soluble gases by the growing droplets were not assessed either.

Another possible bias is that organics in particles retard water uptake by particles [Feingold and Chuang, 2002], which prevents particles in the CCNC column reaching the critical droplet diameter in the residence time of < 13 s. The same mechanism is probably not important in the HTMDA part because the kinetic study of hygroscopic growth of urban aerosol particles in Mexico City shows that the fraction of particles whose time scale of hygroscopic growth is longer than 2-3 s is only <2% for 50 and 100 nm particles [Chuang, 2003].

3. Results and Discussion

3.1 General characteristic of the atmospheric aerosol conditions

The primary objective of this study is to assess the relationship between the hygroscopicity and CCN activity of atmospheric particles, based on HTDMA-CCNC measurements for urban aerosols over Tokyo. The general characteristics of the hygroscopicity and CCN activity, as well as the chemical compositions of aerosol particles during the investigation is briefly presented in this section.
3.1.1 Chemical compositions

Table 2 summarizes the means and ranges of the relative abundances of major chemical species that were obtained by the AMS for particles whose $d_{va}$ ranged from 50 to 200 nm. As presented in Table 2, organics is the dominant compound class (mean: 54%). Such high abundances of organics were also observed in previous AMS studies in Tokyo [Takegawa et al., 2006], and are interpreted as a result of the large contribution of motor vehicle emissions. The AMS spectra indicate the presence of both hydrocarbon-like and oxygenated organics (see section 3.6); the former is mainly primary in origin whereas the latter is secondary [Zhang et al., 2005a]. The sums of water-soluble inorganic ions (NO$_3^-$, SO$_4^{2-}$, Cl$^-$ and NH$_4^+$) are 23% on average. The ratio of organics to water soluble inorganic ions is on average 2.8. The dominance of organic components suggests their important effect on the CCN activity of urban aerosol particles.

3.1.2 Hygroscopic growth factor

Figure 3 presents the averaged distribution of hygroscopic growth factor during the investigation, for particles whose dry diameters were 100 nm. Hygroscopicity $B$ was also calculated as a function of humidified particle diameters and is presented at the top of Figure 3. As shown in Figure 3, particle growth of mono-dispersed particles ($d_{mob,dry} = 100$ nm) by the addition of water vapor leads to a bimodal distribution. This indicates that aerosol particles are externally mixed, i.e., chemical compositions are different from particle to particle. The bimodal distribution is similar to those reported for the urban atmosphere [Heintzenberg, et al., 1998, Gasparini et al., 2004]. The deviation of the distribution presented as the hatched area suggests that the relative abundance of particles in more and less hygroscopic modes, and also those in between, varied substantially depending on the time period during the investigation.
The mode diameter of less-hygroscopic particles after humidification was nearly equal to the dry diameter. The VTDMA shows that less-hygroscopic particles were less volatile, which suggests that the less hygroscopic particles were mainly composed of elemental carbon. The mode of hygroscopicity of more hygroscopic particles ($B \sim 0.2-0.4$) was substantially lower than the hygroscopicity of pure (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ ($B = 0.5$ for both compounds). Further, the number fraction of particles whose hygroscopicities corresponded to that of pure (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ were negligibly small. Based on this result as well as the chemical composition of particles (Table 2), it is concluded that the more-hygroscopic particles are composed of an internal mixture of organics and inorganic salts such as ammonium sulfates and nitrates.

### 3.1.3 CCN size distribution

Figure 4 presents examples of CN and CCN size distributions averaged from November 14 to 15 at supersaturation of 0.22, 0.55, 0.82 and 1.3%. As shown in Figure 4, the range of dry diameters classified by DMA1 in this study (30-200 nm) cover the dominant particle size ranges of CCN during this study. While the CCN/CN ratio starts to decrease toward the smaller particle diameters below $d_{mob,dry} = 200$ nm, the mode diameters of the CCN number distributions were smaller, at around 100-150 nm. This is because the CN distribution has a maximum in the 30-100 nm range. This suggests that the decreasing trend of the CCN/CN ratio toward smaller particle diameter is compensated for by the increasing trend in particle numbers. The total CCN number (integrated area in Figure 4) is thereby sensitive to changes in critical dry diameters for the CCN, suggesting the importance of chemical compositions that control the critical activation dry diameters by regulating hygroscopicity $B$ and surface tension $\sigma$ (and $A$) in Equation 3.
3.2 CCN/CN ratios for particles with different hygroscopicity

Using the HTDMA-CCNC system, the CCN/CN ratios were obtained for four different hygroscopic growth factors (or hygroscopicities) of ambient particles. Figure 5 summarizes all the data of the CCN/CN ratios collected during the sampling period. The ratios were measured under the conditions of (1) hygroscopic growth factors of 1.00, 1.11, 1.24 and 1.38, (2) dry particle diameters of 30, 50, 80, 100, 150 and 200 nm, and (3) RH in the HTDMA of 83 and 89%. Figure 5 clearly shows that the CCN/CN ratios strongly depend on the conditions of supersaturation, hygroscopicity, and dry particle diameters. For instance, for 30 nm particles under the RH condition of 83% in the HTDMA (Figure 5a), significant numbers of CCN were observed only at the highest supersaturation of 1.3%, and hygroscopicity above 1.24. In the case of 50 nm particles (Figure 5b), the spectra of CCN/CN ratios versus hygroscopicity are clearly different from those of 30 nm particles; more CCN was observed for each hygroscopicity and supersaturation than in the case of 30 nm particles. For the particle diameters ≥80 nm, the CCN/CN ratios with hygroscopic growth factor \( g \) ≥ 1.11 were almost unity except for the case of supersaturation at 0.22%. For particles whose dry diameters were 150 and 200 nm, the CCN/CN ratios with \( g \geq 1.11 \) were observed to be unity under all supersaturation conditions (0.22-1.3%).

In general, larger particles are more CCN active than smaller particles (Figures 5a-e). This is consistent with Köhler theory; the more the amount of solute, the larger the resulting droplet diameter (Raoult effect) becomes, being in favor of the CCN activation in terms of the surface tension (Kelvin) effect. Furthermore, it is also evident that particles with higher hygroscopic growth factor \( g \) are more CCN active than those with lower \( g \). The higher growth factor means higher hygroscopicity \( B \), leading to lower critical supersaturation as written in Equation 3.

Limited numbers of data were also collected under the condition of 89% RH in the
HTDMA (Figures 5g and h). The results indicate that the spectra of the CCN/CN ratios versus hygroscopic growth factor for various supersaturations obtained for 50 and 100 nm particles were generally lower than those obtained at 83% RH (Figures 5b and 5d). Although the CCN/CN ratios should not always be the same at different time periods, this trend can be explained by the theory that particles with some hygroscopicity show larger hygroscopic growth factor \( g \) at higher RH in the HTDMA.

3.3 Time series of the CCN distribution as a function of hygroscopicity

Based on the method described in the experimental section, semi-continuous distributions of CCN numbers as a function of hygroscopic growth factor \( g \) were calculated. Figures 6a-c present temporal variations of the CN and CCN distributions as a function of \( g \) for 100 nm particles on November 10-12. The z-axis unit is \( dV \) (particle cm\(^{-3}\))/dlog \( g \), and the particle numbers integrated along the y-axis are equal to those at the inlet of DMA2. Since the transfer function of DMA1 does not change with time, the integrated number is proportional to the number of 100 nm particles in the atmosphere. Chemical compositions of aerosol particles obtained by the AMS (50 nm < \( d_{ca} < 200 \) nm) are also presented in Figure 6d, as estimates of the compositions of particles at \( d_{mob,dry} = 100 \) nm.

Figure 6a shows the number distribution of aerosol particles (CN) as a function of hygroscopic growth factor \( g \). As was presented in Figure 3, bimodal distributions were observed, one for less-hygroscopic and the other for more-hygroscopic particles. The increase in the number concentrations of both particles in the time periods 22:00, November 10 to 12:00, November 11 and 3:00-19:00, November 12 is in accordance with the aerosol mass change detected by the AMS (Figure 6d), supporting the validity of the HTDMA measurements. A sharp increase in the numbers of more-hygroscopic particles (\( g \sim 1.4 \)) at around noon on November 11 (Figure 6a) is coincident with the increase in the mass of SO\(_4^{2-}\).
and NO$_3^-$ (Figure 6d). The number concentrations of less-hygroscopic particles positively correlate with that of the estimated elemental carbon in Figure 6d. This is consistent with the result that more-hygroscopic particles are composed of non-refractory components, whereas less-hygroscopic particles are mainly composed of non-volatile components [Kuwata et al., 2006]. As explained in section 3.1.2, the hygroscopic growth factor of more-hygroscopic mode particles ($g = 1.2-1.4$) were substantially lower than those of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ ($g\sim1.5$), indicating that organics whose hygroscopicity is lower than inorganic salts are major components in more-hygroscopic mode particles. In particular, during the time period from 23:00, November 10 to 7:00, November 11, a fraction of the particles whose hygroscopic growth is intermediate (1.1-1.2) increased, suggesting that the organic fraction became substantial during the time period.

Number distributions of CCN, instead of CN, as a function of hygroscopic growth factor $g$ are novel datasets that were obtained for the first time by our newly developed HTDMA-CCNC system. Figures 6b and 6c present CCN distributions at 0.22% and 0.55% supersaturation, respectively, as a function of hygroscopic growth factor $g$. In the case of 0.22% supersaturation (Figure 6b), some fraction, but not all of the more-hygroscopic particles are detected as CCN. In contrast, almost no particle was detected as CCN for particles in the less-hygroscopic mode. In the case of 0.55% supersaturation (Figure 6c), the numbers of CCN are greater than those at 0.22% supersaturation. In this case, some particles in the less-hygroscopic mode were detected as CCN as well. As explained in section 3.2 and Figure 5, the observed trends in CCN activity between more- and less-hygroscopic particles are consistent with Köhler theory. Figures 6b and 6c further suggest that variation in particle numbers in the atmosphere (Figures 6a and 6d) is also an important factor regulating CCN numbers. For instance, an increase in particle numbers in the more-hygroscopic mode (e.g., at noon on Nov. 11) leads to the increase in CCN numbers shown in Figures 6b and 6c. By
contrast, the increase in less-hygroscopic mode particles, shown as red areas in Figure 6a, does not contribute to an increase in CCN numbers. These results indicate the importance of hygroscopicity for the variation of CCN numbers in the atmosphere.

The data shown in Figures 6a-d are also presented in Figures 7a-d by normalizing the particle numbers. In the figures, the relative abundances of CN and CCN between more- and less-hygroscopic particles can be seen more clearly. On the normalized distribution basis, the CN and CCN fraction at around $g = 1.4$ from 11:00, November 11 to 1:00, November 12 is significant, being consistent with the increase in SO$_4^{2-}$ mass fraction shown in Figure 7d.

3.4 CCN activity as a function of particle hygroscopicity

The number distributions of CCN as a function of hygroscopicity are subjected to the model assessment using Equations 1-3, to clarify whether or not the hygroscopicity measured by the HTDMA can explain the CCN activity of particles. The limitation of this assessment is that the prediction of CCN numbers based on Köhler theory strongly depends on the estimate of the supersaturation condition in the CCN counter which, as explained in the experimental section, is basically based on the KP approach (see section 2.5). However results from K2005 are also discussed in this section.

Among the obtained datasets, we have found that the degree of agreement between the models and the measurements is substantially different from sample to sample. First we present a case in which the CCN spectra as a function of hygroscopicity are well explained by Köhler theory on the assumptions that (1) the surface tension is equal to that of pure water, (2) the hygroscopicity at 83% is same as that at supersaturation RH, and (3) KP is appropriate for the prediction of CCN numbers (section 3.4.1). We also present another case in which the deviation of the measured CCN spectra from that predicted with the above assumptions is relatively large (section 3.4.2). Possible errors associated with particle morphology (section
3.4.3) and non-constant surface tension and hygroscopicity under supersaturation conditions (section 3.4.4) are also discussed. Note that no assumption about the chemical composition is necessary for the quantitative discussion in this section, and that it is solely based on the theoretical relationship between hygroscopic growth factor $g$, hygroscopicity $B$, and critical supersaturation $s_c$.

3.4.1 Case 1: The base model predicts the CCN activity well

Figures 8a-c present number distributions of both aerosol particles (CN) and CCN as a function of hygroscopic growth factor on November 15, 2004. Particles whose dry diameters were 80, 100 and 150 nm were humidified to 83% in the HTDMA, and CCN at 0.22% supersaturation is presented here. As presented in Equations 1-3, if the dry particle size, supersaturation RH, and the surface tension are provided, we can calculate the minimum hygroscopicity $B$ required for particles to behave as CCN. Further, Equations 5 and 6 give the hygroscopic growth factor $g$ corresponding to the thresholds of $B$. In Figures 8a-c, the thresholds of $B$ and $g$ calculated based on the assumptions above are presented as vertical thick lines. The ranges of systematic errors, which are associated with that of RH ($\leq 2\%$), are presented with dotted vertical lines. The thresholds of $B$ (and $g$) are 0.48 (1.48), 0.24 (1.30), and 0.072 (1.11) for 80, 100 and 150 nm particles, respectively. As written above, three assumptions are made in the calculation. First, the hygroscopicity measured at 83% RH by the HTDMA is assumed to well represent that for the supersaturation condition (i.e., $B_{83}/B_{ss}=1$). It should be noted that this assumption leads to some systematic bias at least for inorganic salts. If the $\phi$-RH relationships of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ are taken into account for particles whose dry diameters are 100 nm, the $B_{83}/B_{ss}$ ratios are 0.79 and 0.66, respectively. We nevertheless assume $B_{83}/B_{ss}$ to be unity as a base model. The second assumption is that the surface tension of pure water at the critical supersaturation, corresponds to $A = 1.0 \times 10^{-3} \mu$m
at 308 K. This is reasonable for most inorganic particles [Brechtel and Kreidenweis, 2000b], whereas it is possibly not correct for some organic/inorganic mixtures [Schulman et al., 1996, Facchini et al., 1999]. The third assumption is the determination of supersaturation in the CCN counter by the KP model.

Taking into account the width of supersaturation RH in the CCN counter, we further estimated the non-stepwise change in the CCN/CN ratios around the threshold of $B$. Widths of supersaturation without correction of the size widths of (NH$_4$)$_2$SO$_4$ particles are used (i.e., values without parenthesis in Table 1). The absence of the size-width correction is reasonable because dry particles classified in DMA1 in the HTDMA also have the same standard deviation in particle diameters. The derived CCN numbers as a function of hygroscopic growth factor $g$ are shown as blue histograms in Figures 8a-c. The error bars represent random errors in the predicted CCN distribution (see section 3.4.2), which however do not include systematic errors (vertical dotted lines). Nearly all of the particles in the more-hygroscopic mode are predicted by the blue histograms. There are some unpredicted CCN at around $g = 1.00$, but their CCN activity is difficult to assess by the approach in this study. Because the main component of these non-hygroscopic particles is estimated to be elemental carbon [Kuwata et al., 2006], they are probably aggregates and have non-spherical shapes. Conversely, it may be reasonable to assume that more-hygroscopic particles are spherical under dry conditions. This is because (1) mixtures of many different organic compounds are not likely to form single non-spherical crystals, (2) even liquid ammonium sulfate particles dried ($d_{mob} < 200$ nm) form nearly spherical particles [Zelenyuk et al., 2006], and (3) electron micrograph study of more-hygroscopic particles classified by HTDMA revealed that they are spherical, not like chain agglomerates or flakes as in the case of less-hygroscopic particles [McMurry et al., 1996]. The validity of this assumption is further discussed in section 3.4.3.
The good agreement between the predicted and measured CCN distributions as a function of $g$ shows that the introduction of surface tension reduction \cite{Facchini et al., 1999} is not necessary for explaining the data presented in Figure 8. Furthermore, $B_{83}$ is nearly equal to $B_{ss}$, which suggests that dissociation and dissolution of organics via the increase in RH from 83% to supersaturation is not necessary either for explaining the measured CCN activity of particles. This result might be in contrast to the fact that $B_{83}/B_{ss}$ for pure (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ particles whose dry diameters are 100 nm are to some extent lower than unity (0.79 and 0.66, respectively). This difference possibly relates to the result that the mass of these inorganic salts measured by the AMS is only half of that of organics, leading to different non-ideal behavior.

With the application of the some other CCN activation models \cite{Kreidenweis et al., 2005}, the threshold $B$ is lower than presented in Figure 8. For instance, if K2005 (see section 2.5) is used to determine the supersaturation in the CCN counter, the supersaturation condition for the experiment shown in Figure 8 is calculated to be 0.28%. This lowers the thresholds of $B$ to 0.29, 0.15 and 0.044 for 80, 100 and 150 nm particles, respectively. In this case, $B_{83}/B_{ss}$ and/or $\Delta\sigma/\sigma$ need to be much larger than unity to match the predicted and measured of the CCN distributions. The $\Delta\sigma/\sigma$ value larger than unity is contradictory to the hypothesis that organics in aerosol particles lower the surface tension \cite{Facchini et al., 1999}. Moreover, it is difficult to reasonably explain $B_{83}/B_{ss}$ being significantly larger than unity, because both the dissolution/dissociation of organics by dilution, and the presence of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ lower the $B_{83}/B_{ss}$ ratio from unity.

It is, however, difficult to conclude that KP gives a better prediction of supersaturation than K2005. In the study by Kreidenweis et al. [2005], K2005 predicts supersaturation similar to some other models, e.g., a model based on literature values of water activity and density of (NH$_4$)$_2$SO$_4$ particles [Tang and Munkelwitz; 1994]. If we assume that K2005 gives a better
prediction, this suggests that our measurement and/or interpretation based on Equations 1-3 are systematically biased. Kinetic limitation of hygroscopic growth [Chuang, 2003; Chan and Chan, 2005] and CCN activation [Chuang et al., 1997], and gas/particle re-equilibration of soluble trace gases in the CCN counter [Laaksonen et al., 1998] are possible explanations, but their magnitudes are unknown. Since there is so far no means for judging which model gives the most accurate estimate of the supersaturation in the CCN counter, we use KP as a base model in this study to avoid the introduction of $B_{83}/B_{ss}$ and a value of $\Delta \sigma/\sigma$ significantly larger than unity. Results from K2005 are also discussed to assess the potential uncertainty of the discussion.

3.4.2 Case 2: Unpredicted CCN fraction is present

In contrast to the results shown in Figures 8a-c, the numbers of CCN larger than that predicted by the assumptions above (i.e., application of KP to determine the supersaturation RH, $\Delta \sigma/\sigma = 0$, and $B_{83}/B_{ss} = 1.0$) were observed over substantial time periods. Figure 9a is an example of such cases for particles whose dry diameters are 100 nm. In this case, the predicted number of CCN particles is only less than half of that measured. Although some multiply charged particles classified in DMA1 [Wiedensohler, 1988] should be detected as CCN active just because of their larger size, the fraction of the multiply charged particles was minor throughout the study (16 ± 3% for 100 nm particles).

Temporal variation of supersaturation (random error: 5%) may in part be responsible for the deviation of the threshold of $B$, but the magnitude may not fully explain the differences in CCN distributions shown in Figures 8 and 9a. Table 3 presents a sensitivity study of thresholds of $B$ and $g$ in the case that the set point of supersaturation is 0.22%. It is shown that the possible random errors in the thresholds of $B$ and $g$ are mainly associated with the random error in $s_c$, and those from other factors, RH and $d_{mob,dry}$ (which relate to the precision of $g$ in...
Table 2), are minor. Change in the threshold of $B$ as a result of changes in $s_c$ from +1 to −1 SD is 20% (= +10.8% − (−9.3%)), whereas the difference in the threshold of $B$ required to explain Figures 8 and 9 are 50%, which corresponds to 5 SD change of $s_c$.

A likely explanation for the discrepancy between the measured and predicted CCN distributions is that either or both of the assumptions of $\Delta \sigma/\sigma = 0$ and $B_{83}/B_{ss} = 1$ are not appropriate in the case presented in Figure 9a. First, if we assume that hygroscopicity $B$ measured using HTDMA is not largely different from that under the supersaturation condition ($B_{83} \approx B_{ss}$), the presence of unexpected CCN suggests that the surface tension of particles could be lower than that of pure water (See possible changes of the threshold for different $\Delta \sigma/\sigma$ values in Figure 9a). Facchini et al., [1999] has suggested based on their fog measurements that surface tension reduction due to organic compounds in aerosol particles could be 25% lower under supersaturation conditions. We applied the 25% decrease in the surface tension, and calculated the shift in the threshold of $B$ and $g$ to be CCN active (Figure 9b). The distribution of predicted CCN as a function $g$ is also recalculated accordingly. As shown in Figure 9b, the decrease in surface tension significantly increases the predicted CCN number, and the majority of the unexpected CCN fraction is explained. Some CCN fraction below the threshold is still not predicted, but such a small fraction may be explained by the presence of multiply charged particles and their non-spherical shapes. Since the relationship between the surface tension reduction and the shift in the threshold was calculated based on a constant $\sigma$ value around the critical droplet diameter (see Equation 3), the relationship is potentially biased if the surface tension is not constant near the critical supersaturation condition. However, the difference is probably negligible as is discussed in section 3.4.4.

The difference in hygroscopicity $B$ under sub- and supersaturated conditions (i.e. $B_{83}/B_{ss} \neq 0$) is also possibly responsible for the unexpected CCN fraction in Figure 9a. The threshold of $B$ on the assumption that $\Delta \sigma/\sigma = -25\%$ (Figure 9b) is equivalent to the change in
hygroscopicity explained by $B_{83}/B_{ss} = 0.42$. Such difference in the hygroscopicity $B$ could be
caused by the RH dependence of the non-ideality term $\nu \phi$ and the degree of dissolution $\varepsilon$

[Schulman et al., 1996]. If the particle is assumed to be composed of an insoluble core and an
$(\text{NH}_4)_2\text{SO}_4$ (or $\text{NH}_4\text{NO}_3$) solution shell, the threshold of $g$ corresponding to 0.22%
supersaturation was calculated to be 1.25 (or 1.23), which fails to explain the CCN
distribution (see Figure 9). The $B_{83}/B_{ss}$ ratios for $(\text{NH}_4)_2\text{SO}_4$ and $\text{NH}_4\text{NO}_3$ in the core-shell
models are 0.81 and 0.66, respectively, which are close to those for pure $(\text{NH}_4)_2\text{SO}_4$ (0.79)
and $\text{NH}_4\text{NO}_3$ (0.66). In addition, if only inorganic salts generally govern $B_{83}/B_{ss}$ as in the
core-shell model, it is difficult to explain the deviation of the $B$ thresholds between Figure 8b
(case 1) and Figure 9b (case 2). Moreover, the influence of inorganic salts on $B_{83}/B_{ss}$ may be
limited because the fraction of sulfate and nitrate in the particles are probably rather small
(Figure 7 and Table 2). Hence, the organic component present in particles is more likely to be
responsible for the low $B_{83}/B_{ss}$ ratio. They may also relate to the variation of the ratio, in
addition to that originating from $\Delta s_c$ (Table 3). If the non-ideality term $\nu \phi$ of organics is
different from inorganic salt, and if the soluble fraction $\varepsilon$ is less than unity for some organics,
the organics significantly affect the RH dependence of hygroscopicity $B$. In this case, change
in the mixing ratios of organics and inorganic salts may lead to the observed variation of
$B_{83}/B_{ss}$. Furthermore, temporal variation of characteristics of organics, e.g., the degree of
oxidation, may also change $B_{83}/B_{ss}$ via changes in $\nu \phi$ and $\varepsilon$.

As explained in the previous section, application of the K2005 model to the prediction
of supersaturation conditions leads to a substantial increase in the predicted CCN numbers. In
the case of the aerosol sample shown in Figure 9, the estimated threshold of $B$ based on
K2005 is 0.15, which gives a prediction similar to Figure 9b. However, as described above,
application of K2005 in turn overpredicts the CCN numbers in the cases in Figure 8, which is
difficult to explain without introducing biases that have not already been taken into account in
3.4.3 Particle morphology

It is useful to assess the potential errors of the prediction of CCN numbers if dry particles classified in DMA1 are not perfect spheres. If particles are non-spherical, the volume equivalent diameter \(d_{ve}\) is smaller than the mobility diameter \(d_{mob}\). Given that dry particles of more-hygroscopic mode are non-spherical or porous and that they are spherical after humidification in the HTDMA, the substitution of \(d_{ve,dry}\) by \(d_{mob,dry}\) as in this study leads to an underestimation of hygroscopicity in sub- and supersaturated conditions. Although the errors in two different conditions in part cancel out in the comparison between \(g\) and \(s_c\), underestimation of the hygroscopicity \(B\) and overestimation of \(d_{ve,dry}\) in Equation 3, overall leads to an overestimation of the critical supersaturation \(s_c\).

As an extreme case for more-hygroscopic particles, we assume that the dynamic shape factor \(\chi\) of dry particles in DMA1 is 1.18, which is for cubic particles whose \(d_{mob,dry}\) is 100 nm [Biskos et al., 2006]. In the case of particles whose apparent \(g\) is 1.30 (equal to the calculated threshold of \(g\) to be CCN active in Figure 8b), \(d_{ve,dry}\) is calculated to be 9% smaller than \(d_{mob,dry}\), which gives errors of +10% in predicted \(s_c\). The error of the predicted \(s_c\) is equivalent to a shift in the threshold of apparent \(g\) from 1.30 to 1.25 (see Figure 8a). Therefore, predicted CCN numbers on the assumption of a potential non-spherical shape is to some extent larger than those presented in Figure 8. However, the shift in the threshold does not fully explain the measured CCN numbers. Further, the error in the prediction of CCN numbers for ambient particles in the more-hygroscopic mode may be smaller, because their shape under dry conditions may be closer to spheres than to cubic particles. This is supported by the result that dry ammonium sulfate particles have a dynamic shape factor in free molecular regime \(\chi\), less than 1.04 for \(d_{mob} < 200\) nm, and that addition of organics to ammonium sulfate particles
further lowers $\chi_v$ [Zelenyuk et al., 2006]. We thereby conclude that the possible nonsphericity of more-hygroscopic particles may have a limited effect on the discussion here. It should be noted, however, that the sensitivity of $s_c$ to the dynamic shape factor $\chi$ is a function of $g$, and that it is significantly high if $g$ is very close to unity with less hygroscopic particles.

3.4.4 Changes in surface tension and hygroscopicity in supersaturation conditions

In section 3.4.2, negative $\Delta \sigma/\sigma$ values and $B_{83}/B_{ss}$ less than unity were introduced to explain the unexpected CCN fraction. The calculation was based on Equation 3; $\Delta \sigma/\sigma$ and $B_{ss}$ are assumed to be constant near the critical supersaturation condition. However, the values of $\Delta \sigma/\sigma$ and $B_{ss}$ of atmospheric particles are not necessarily constants in supersaturation conditions. The errors associated with this simplification are assessed in this section.

As a preliminary assessment of the non-constant surface tension, we applied the relationship between $\sigma$ and Water Soluble Organic Carbon (WSOC) concentration presented by Facchini et al. [1999]. In this model, as the droplet diameter increases with humidification, the WSOC concentration decreases by the dilution in particle liquid water. The surface tension then increases monotonically, which eventually approaches the surface tension of pure water. We estimated the $\sigma - d_{ve}(RH)$ relationship by assuming that WSOC is completely dissolved regardless of the amount of liquid water. Surface tension reduction by insoluble organic films, micelle formation [Tabazadeh, 2005], and the effect of surfactant partitioning to the Raoult effect [Sorjamaa et al., 2004] are not considered here. In the case that $\Delta \sigma/\sigma$ is fixed at $-25.0\%$ near the critical supersaturation condition and that $d_{mob,dry} = 100$ nm and $B_{ss} = B_{83} = 0.265$, the critical supersaturation $s_c$ was calculated from Equation 3 to be $0.14\%$. Next we calculated $s_c$ numerically, applying $\Delta \sigma/\sigma$ as a function of $d_{ve}(RH)$ [Facchini et al., 1999]. The WSOC fraction in particles was adjusted so that the same critical supersaturation condition ($0.14\%$) was established without changing $d_{mob,dry}$, $B_{ss}$ and $B_{83}$ values. In this numerical calculation,
\[ \Delta \sigma/\sigma \] under critical supersaturation conditions was calculated to be \(-25.4\%\). The difference of \[ \Delta \sigma/\sigma \] in the two model cases (with constant and variable \( \sigma \)) is very small (0.4\%), supporting the validity of using Equation 3 with constant \( \sigma \) in the supersaturation condition. It should be noted, however, that the error in \[ \Delta \sigma/\sigma \] depends on the \( \sigma - d_{ve}(\text{RH}) \) relationship applied, and the error in \[ \Delta \sigma/\sigma \] under supersaturation conditions is larger or smaller if the other model relationships are applied [e.g., Li et al., 1998; Sorjamaa et al., 2004]. Qualitatively, the error of the prediction based on Equation 3 could be larger if the slope of the function \( \sigma = f(d_{ve}(\text{RH})) \) near the supersaturation condition is larger.

Similar to the case of non-constant surface tension, if the hygroscopicity \( B \) near the critical supersaturation condition is not constant, application of Equation 3 leads to the error in the \( s_c - B_{SS} \) relationship. The perturbation is negligible in the cases of the insoluble core - (NH\(_4\))\(_2\)SO\(_4\) (or NH\(_4\)NO\(_3\)) shell model; The errors in \( B_{SS}/B_{SS} \) for fixed \( s_c \) (0.22\%) is less than 0.01. However, the magnitude of the error cannot be assessed for atmospheric particles because of the lack of information about the \( B - d_{ve}(\text{RH}) \) relationship.

### 3.5 Role of organics in the CCN numbers

For the aerosol particles measured in this study, the CCN number concentrations at the inlet of DMA2 were calculated by integrating the measured CCN number distributions as a function of hygroscopic growth factor \( g \) (e.g., the red histograms in Figures 8 and 9). Further, CCN concentrations are predicted based on the modeled CCN – \( g \) relationship (e.g., the blue histograms in Figures 8 and 9a and the green histogram in Figure 9b). In Figure 10, measured and predicted CCN number concentrations are plotted for all the samples when the dry particle diameters were 100 nm and the supersaturation condition was 0.22\%. Here results from both KP and K2005 are presented for comparison. In each figure, the predicted CCN number concentrations are plotted for three different cases; the reduction of surface tension
$\Delta \sigma/\sigma$ is 0, -12.5, and -25% whereas $B_{83}/B_{SS}=1$. They are equivalent to the assumptions that

$B_{83}/B_{SS}$ are 0.42, 0.67 and 1 in the case $\Delta \sigma/\sigma=0$. In Figure 10a (KP), most of the data points for the assumptions $\Delta \sigma/\sigma = 0$ and $B_{83}/B_{SS}=1$ are between the 1:1 and 1:2 lines, indicating that this base case predicts about 50-100% of the CCN present, depending on the time period. The average of the ratios of predicted for the measured CCN numbers ($N_{CCN,\text{pred}}/N_{CCN,\text{meas}}$) in the base case is 0.59 (1SD: 0.24). Few data points are above the 1:1 line, suggesting that any mechanism to reduce the CCN activity relative to the base model ($\Delta \sigma/\sigma = 0$ and $B_{83}/B_{SS}=1$) is unnecessary. The predicted CCN on the assumption that $\Delta \sigma/\sigma = -25\%$ (or $B_{83}/B_{SS} = 0.42$) are between the 1:1 and 2:1 lines. In this case, the average of $N_{CCN,\text{pred}}/N_{CCN,\text{meas}}$ is 1.68 (one standard deviation: 0.57).

In the case of K2005 (Figure 10b), CCN numbers are overpredicted for many of the samples. In the base case ($\Delta \sigma/\sigma = 0$, $B_{83}/B_{SS} = 1$), many of the data points are between the 1:1 and 2:1 lines. The reduction of surface tension ($\Delta \sigma/\sigma < 0$), and dissolution/dissociation by the dilution ($B_{83}/B_{SS} < 1$) further enhance the discrepancy between the predicted and measured CCN numbers. As explained above, the $N_{CCN,\text{pred}}/N_{CCN,\text{meas}}$ ratio higher than unity for the base case ($\Delta \sigma/\sigma = 0$, $B_{83}/B_{SS} = 1$) is less realistic than that less than unity, and hence suggests systematic errors in the measurement/analysis and/or K2005. In any case, the sample-to-sample deviation of the $N_{CCN,\text{pred}}/N_{CCN,\text{meas}}$ ratios in the base case is similar for both KP and K2005.

Based on the difference between measured and predicted CCN number concentrations, we calculated the possible reduction of surface tension in the case that $B_{83}/B_{SS} = 1$. Figure 11 plots the frequency distribution of samples as a function of $\Delta \sigma/\sigma$. Here only the result from KP is presented. Our data suggests that the surface tension reductions were in the range of $-25\%$ to $+10\%$ during the sampling period. The mode values of the frequency were from $-15\%$ to -10%, and 76% of samples (29 among 38) were from $-20\%$ to -5%. Additionally, the
The $B_{83}/B_{SS}$ ratio, in the case that reduction of surface tension is negligible, is presented in the top axes. The difference in $B_{83}/B_{SS}$ is up to two fold, and the relative standard deviation is 19%. This deviation is about a factor of two larger than that estimated from random errors in the measurement (see Table 3).

Although there may be room for discussion on the uncertainty of the supersaturation conditions in the CCN counter, the results in Figures 10 and 11 are in agreement with the hypothesis that characteristics originating from organic compounds in particles influence the CCN activity of atmospheric particles. It should be noted that water-soluble organics also contribute to the CCN activity via the solute effect [Dick et al., 2000], and contributions of water-soluble organics might be important even in the case of Figure 8. Our HTDMA-CCNC experiment suggests that, in addition to the solute effect of water-soluble organics, other factors associated with organics could also affect the CCN activity of urban aerosol particles.

### 3.6 Chemical compositions and the CCN activity

As discussed above, comparison between predicted and measured CCN numbers strongly depend on the models used to predict supersaturation in the CCN counter, which limits the interpretation of the data. On the other hand, the deviation of $N_{CCN,pred}/N_{CCN,meas}$ from its average is not sensitive to the applied model (KP or K2005). Here we present a preliminary assessment of the relationship between $N_{CCN,pred}/N_{CCN,meas}$ and chemical compositions of more-hygroscopic mode particles estimated from the AMS data. Chemical components other than EC in Table 2 are assumed to be entirely present in more-hygroscopic mode particles. It should be noted that this assumption is not necessarily true because some fraction may have been associated with less-hygroscopic particles, although heating at 400 °C in VTDMA did not lead to significant change in the $d_{mob}$ of less-hygroscopic particles [Kuwata et al., 2006]. In this analysis, organic components are subdivided into
hydrocarbon-like organics and oxygenated organics according to the analytical procedure of
the AMS data in Zhang et al. [2005b].

Table 4 presents correlations of $N_{CCN,pred}/N_{CCN,meas}$ with ratios of different chemical
components. All of the correlations presented in Table 4 are statistically significant. In
particular, the correlation between $N_{CCN,pred}/N_{CCN,meas}$ and the ratio of the hydrocarbon-like
organic mass (HOM) (or oxygenated organic mass (OOM)) to the total organic mass (OM)
was substantial, implying a relationship between CCN activity and the characteristics of the
organic compounds. The presence of correlations between $N_{CCN,pred}/N_{CCN,meas}$ and chemical
composition supports the interpretation that the observed variation of the $N_{CCN,pred}/N_{CCN,meas}$
ratio is not merely random noise caused by fluctuations of $s_c$ and other variables.

The correlation between HOM/OM (or OOM/OM) and $N_{CCN,pred}/N_{CCN,meas}$ indicates
that the underprediction of the CCN numbers are significant for samples whose HOM/OM is
relatively large. Although the correlation does not necessarily mean that the fraction of
hydrocarbon-like organics is casually associated with CCN activity, it may be worth noting
that the relationship is consistent with the hypothesis of the potential effects of organics on
CCN activity (sections 3.4 and 3.5). Possible explanations are that hydrocarbon-like organics
are associated with surface-active organics, and/or that hydrocarbon-like organics contain
slightly soluble compounds that substantially enhance partitioning in the aqueous phase under
RH conditions above 83%. Because the HTDMA-CCNC and the AMS did not measure
exactly the same fraction of atmospheric particles, the quantitative relationship has not been
assessed in more detail in this study. More experiments are required to clarify the linkages
between organic composition and CCN activity using the HTDMA-CCNC system coupled to
the AMS.

3.7 Comparison with previous CCN studies and future perspectives
As explained in the introduction section, hygroscopicity and CCN activity of atmospheric aerosol particles have been measured simultaneously in several field studies [Brechtel and Kreidenweis, 2000a; Zhou et al., 2001; Dusek et al., 2003; Roberts et al., 2004; Rissler et al., 2005]. Some studies overpredicted CCN concentrations by about 30% [Zhou et al., 2001; Dusek et al., 2003], whereas Rissler et al. [2004] suggested that the application of the measured hygroscopicity at 90% RH using HTMDA and of the surface tension of pure water to the Köhler equation well predict the measured CCN numbers within a 25% error. Although our study does not give a full answer to the potential difference in measured and predicted CCN numbers, results in Figures 10 and 11 suggest that factors associated with organics cause some deviation of the measured CCN numbers from prediction. This implication is due to the high sensitivity of the CCN numbers to the factors associated with organics in our HTDMA-CCNC analysis. Different from previous studies, CCN activity and hygroscopicity of particles have been investigated for specific particle sizes, and CCN activity has been assessed for particles with specific hygroscopicity.

As discussed in this paper, the non-ideality of the droplet solution, i.e., RH dependence of hygroscopicity $B$ is an important factor for the prediction of CCN activity from HTDMA data. In previous studies, CCN activity has been typically estimated from the HTDMA data assuming a mixture of an inorganic solution and an insoluble core. In this case, the non-ideality of the solution is taken into account by applying a $\phi$-RH relationship of known inorganic compounds, such as (NH$_4$)$_2$SO$_4$. However, such RH dependence of $\phi$ (or $B$) is basically not assumed for the prediction of CCN in this study. This is to simplify the discussion, but also because non-ideality of the organic-inorganic mixture is not necessarily similar to that of major inorganic salts such as (NH$_4$)$_2$SO$_4$. Activity coefficients of water in many organic solutions are more than unity, whereas those for (NH$_4$)$_2$SO$_4$ are less than unity, which means that even the sign of $\Delta B/\Delta RH$ between sub- and supersaturated conditions.
depends on the solute compounds. Therefore, it is possible that the non-ideal behavior of
ambient particles are substantially different from pure inorganic salts, in particular when the
organic fraction is very large as observed in this study.

A novel approach to evaluate the relationship between hygroscopicity at sub- and
supersaturated conditions and CCN activity using HTDMA data has recently been proposed
by Kreidenweis et al. [2005]. Their approach was similar to that in this study, but they
proposed to extrapolate the hygroscopicity $B$ measured at subsaturation RH (up to 95%) to
that at supersaturation, using a polynomial function of water activity obtained by the HTDMA.
Although their approach does not clarify the degree of dissolution/dissociation that occurs
above the upper limit of RH in the HTDMA, this approach is worth investigating in future
studies using the HTDMA-CCNC system to improve the prediction of hygroscopicity $B$ at
supersaturation conditions.

This study shows that deviation in CCN activity caused by surface tension reduction
ranging from $\Delta\sigma/\sigma = -25\%$ to $0\%$ is, at least theoretically, detectable with the precision of
the HTDMA-CCNC measurements. Although the HTDMA-CCNC approach does not give
full information on the surface tension of particles, this approach may compensate for the
weakness of the bulk surface tension measurement [Facchini et al., 1999; Facchini et al.,
2000], where the difference in chemical characteristics between externally mixed particles is
completely lost. In addition, surface tension measured in the bulk sample is not necessarily
equal to that at the particle surface, because some insoluble surfactants may accumulate at the
interface and the difference in surface/volume ratios between submicron particles and bulk
solutions might lead to a large difference in the surface tension. In this sense, the
HTDMA-CCNC measurements, which may give a lower limit to the surface tension, is a
promising means for measuring the surface tension in the form of aerosol particles.
4. Summary

A newly developed HTDMA-CCNC system was deployed for the field measurement of hygroscopicity and CCN activity of urban aerosol particles in Tokyo in November 2004. The CCN activity was successfully measured for particles with specific dry diameters and hygroscopicity in externally mixed aerosols. This approach made it possible to assess the relationship between hygroscopicity and CCN activity in detail, in a novel manner that has not been conducted in previous field studies using a HTDMA and a CCN counter.

The CN and CCN spectra as a function of hygroscopic growth factor clearly showed that hygroscopicity of particles, which is regulated by their chemical composition, is a critically important factor for the CCN activity of urban aerosol particles. Furthermore, the spectra also showed that increases in the particle size and the supersaturation make less hygroscopic particles CCN active. The measured CCN distribution as a function of hygroscopicity is quantitatively evaluated based on Köhler theory, and it has been found that the predicted CCN activity – hygroscopic growth factor relationship based on the Köhler model in many cases does not fully explain the measured CCN numbers. Furthermore, variations of the ratios of the predicted to measured CCN numbers are larger than predicted from the precision of the supersaturation condition in the CCN counter, in terms of precision and trueness, may need further evaluation, the results are reasonably explained if factors other than the hygroscopicity of particles under subsaturated conditions are responsible for the measured CCN activity. The factors may include reduction of surface tension due to organics, dissolution/dissociation of slightly water-soluble organics, and the difference in non-ideality between organics and inorganic salts. These factors associated with organics potentially contribute to the CCN activity of urban aerosol particles.

Chemical compositions obtained by the AMS operated in parallel to HTDMA-CCNC
system gave additional information that supports our interpretation of the observed relationship between hygroscopicity and CCN activity. Temporal variations of the spectra of hygroscopicity and CCN numbers were confirmed to be in accordance with those of chemical compositions. Furthermore, a correlation between organic composition and the ratios of predicted to measured CCN numbers was found to be present. This implies that the variation of the ratios of the predicted to measured CCN numbers are not noise, and that the composition of organics is responsible for the variation.

In current cloud models, CCN activity of particles is in many cases regulated only by their size. Many field, laboratory and modeling studies are being conducted to assess the importance of the chemical compositions of particles for cloud processes. Our study demonstrates that the HTDMA-CCNC system deployed for field experiments is a promising tool for assessing the importance of chemical characteristics. Future studies using the HTMDA-CCNC system may contribute to extending our knowledge of the relationship among chemical composition, hygroscopicity and CCN activity of atmospheric aerosol particles.

Acknowledgements  This study is in part supported by the Ministry of Education, Science, Sports, and Culture through Grants-in-Aid 14204055 and 14658149.
References


Feingold, G. and P. Y. Chuang (2002), Analysis of the influence of film-forming compounds

Gasparini, R., R. Li, and D. R. Collins (2004), Integration of size distributions and size-resolved hygroscopicity measured during the Houston Supersite for compositional categorization of the aerosol, *Atmos. Environ.*, 38, 3285-3303.


1023 1859-1866.
1034 Novakov T., and J. E. Penner (1993), Large contribution of organic aerosols to cloud-condensation-nuclei concentrations *Nature*, 365, 823-826.


Zhang, Q., M. R. Canagaratna, J. T. Jayne, D. R. Worsnop, and J. L. Jimenez (2005c), Time-


Figure Captions

Figure 1.  Diagram of the experimental setup. The CCN counter was connected to the HTDMA in parallel to the CN counter. The AMS was operated in parallel to the HTDMA. The third DMA (DMA3) and the CN counter connected with the 400°C heater (volatility TDMA) were for quantifying non-volatile components [Kuwata et al., 2005]. Key: SG, Silica Gel; MS, Molecular Sieve; SMPS, Scanning Mobility Particle Sizer; DMA, Differential Mobility Analyzer; CN, Condensation Nuclei; CCN, Cloud Condensation Nuclei; CPC, Condensation Particle Counter.

Figure 2.  (a) An example of the measured distributions of CN (white histogram) and CCN (shaded histogram) as a function of hygroscopic growth factor $g$. (b) The ranges of the hygroscopic growth factor of the particles when CCN numbers were measured at the four fixed set points of hygroscopic growth factors (1.00, 1.11, 1.24 and 1.38). (c) Weighting functions to calculate CCN distributions.

Figure 3.  Normalized distribution of hygroscopic growth factor $g$ at 83% RH for 100 nm particles during the study. Mean distributions (thick solid line) and the ranges within one standard deviation (shaded area) are presented.

Figure 4.  Size distributions of CN and CCN for (a) 0.22%, (b) 0.55%, (c) 0.82%, and (d) 1.3% supersaturations. Size distributions averaged from 23:00, 11/14 to 21:00, 11/15 in 2004 are presented. CCN distributions were determined from CCN/CN ratios measured for 30, 50, 80, 100, 150, and 200 nm particles and their interpolation. In the case of (a) 0.22% supersaturation, the CCN/CN ratio was extrapolated toward larger diameters on the assumptoim that the CCN/CN ratio is unity for 300 nm particles.

Figure 5.  The CCN/CN ratios measured for hygroscopic growth factors of 1.00, 1.11, 1.24, and 1.38. The hygroscopic growth factors were measured at (a-f) 83% and (g and h) 89% RH in the HTDMA, respectively. The initial dry diameters of particles were (a) 30, (b and g) 50, (c) 80, (d and h) 100, (e) 150 and (f) 200 nm. Supersaturation conditions in the CCN counter were 0.22% (open circles), 0.55% (solid triangles), 0.82% (open squares), and 1.3% (solid diamonds).
Figure 6. Temporal variations of the number distributions of (a) CN, (b) CCN at 0.22% supersaturation, and (c) CCN at 0.55% supersaturation as a function of hygroscopic growth factor \( g \). Particle numbers are for sample aerosols entering DMA2. (d) Mass concentrations of inorganics and organics measured using the AMS (\( d_{\text{va}} \): 50 - 200 nm).

Figure 7. Temporal variations of the normalized distributions of (a) CN, (b) CCN at 0.22% supersaturation, and (c) CCN at 0.55% supersaturation as a function of hygroscopic growth factor \( g \). (d) Relative abundances of inorganics and organics measured using the AMS (\( d_{\text{va}} \): 50 - 200 nm).

Figure 8. Distributions of CN (black) and CCN (red) numbers as a function of hygroscopic growth factor \( g \) (or hygroscopicity \( B \)) for the sample on November 14, 2004. The initial dry diameters were (a) 80 nm, (b) 100 nm, and (c) 150 nm. Predicted CCN distributions by assuming \( \Delta \sigma/\sigma = 0\% \) have been superimposed as blue histograms. Error bars on the predicted distributions represent the random errors, which is mainly associated with the precision of \( s_c \) (see section 3.4.2 and Table 3). The vertical solid lines are the lower limits (thresholds) of \( g \) and \( B \) to be CCN at 0.22% supersaturation. The systematic errors of the thresholds are shown as vertical dotted lines. Hygroscopicity \( B \), and the possible change in the threshold by that of surface tension are shown as extra x-axes on the figures. Supersaturation was calculated based on the KP model \([\text{Köhler, 1936; Pitzer and Mayorga, 1973}]\). Results based on K2005 \([\text{Kreidenweis et al., 2005}]\) are not shown here but discussed in the text. See section 2.5 for details of the KP and K2005 models.

Figure 9. Distributions of CN (black) and CCN (red) numbers as a function of hygroscopic growth factor for 100 nm particles for the sample on November 10, 2004. Predicted CCN distributions by assuming (a) \( \Delta \sigma/\sigma = 0\% \) and (b) \( \Delta \sigma/\sigma = -25\% \) were superimposed as (a) blue and (b) green histograms, respectively. Error bars on the predicted distributions represent the random errors. The vertical thick and dotted lines are the lower limits (thresholds) of hygroscopicity \( B \) (and hygroscopic growth factor \( g \)) to be CCN at 0.22% supersaturation and the range of the systematic error, respectively. Hygroscopicity \( B \), and the possible change of the threshold by that of surface tension are shown as extra x-axes on the figures. Supersaturation was calculated based on the KP model. Results based on K2005 are not shown but discussed in the text.
Figure 10. Plots of predicted versus measured CCN concentrations on the assumptions that $B_{83}/B_{ss}=1$ and reductions of surface tension, $\Delta \sigma / \sigma$, are 0% (open blue squares), -12.5% (solid green circles), and –25% (solid red squares). Results from two different predictions of supersaturation conditions based on (a) the KP [Köhler, 1936; Pitzer and Mayorga, 1973] and (b) the K2005 [Kreidenweis et al., 2005] models are presented. These plots also correspond to the case where $\Delta \sigma / \sigma = 0\%$ and $B_{83}/B_{ss}$ are 1.0 (open blue squares), 0.67 (solid green circles), and 0.42. The 1:2, 1:1 and 2:1 lines are also presented in the figure. The CCN concentrations are for sample aerosols entering DMA2 of the HTDMA system. All the multiply charged particles are assumed to be CCN active, and omitted from both measured and predicted CCN numbers. Error bars represent the systematic errors, which are associated with the trueness of the RH measurement ($\leq 2\%$) in DMA2. The magnitude of the random errors in the predicted CCN numbers (not shown) is similar to the range of the systematic errors presented.

Figure 11. Frequency distribution of 100 nm-particle samples as a function of $\Delta \sigma / \sigma$, on the assumption that $B_{83}/B_{ss}=1$. The $B_{83}/B_{ss}$ value is also shown at the top of the graph on the assumption that $\Delta \sigma / \sigma = 0\%$. This figure is based on the calculation of supersaturation using the KP model. The value of $\Delta \sigma / \sigma (B_{83}/B_{ss}=1)$ corresponding to $N_{CCN\_pred} / N_{CCN\_meas} = 1$ for each sample was obtained by linear interpolation of the relationship between $N_{CCN\_pred} / N_{CCN\_meas}$ and $\Delta \sigma / \sigma$ at $\Delta \sigma / \sigma = 0\%$, -12.5% and –25% (see Figure 10). The systematic error averaged for all samples is calculated from the trueness of the RH measurement in DMA2, and is presented in the top-left of the figure. Note that $B_{83}/B_{ss}$ of pure $(NH_4)_2SO_4$ is 0.79.
<table>
<thead>
<tr>
<th>Variables</th>
<th>Random error (^a) (Precision)</th>
<th>Systematic error (^b) (Trueness)</th>
<th>Width (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Measured Variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN count</td>
<td>1–4% (^b)</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>CCN count</td>
<td>2–10% (^b)</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>(d_{mob}) classified by DMA1</td>
<td>1%</td>
<td>Calibrated with DMA2</td>
<td>4%</td>
</tr>
<tr>
<td>(d_{mob}) classified by DMA2</td>
<td>1%</td>
<td>Used as a reference DMA, calibrated using PSL particles</td>
<td>4%</td>
</tr>
<tr>
<td>Supersaturation</td>
<td>5% (^c)</td>
<td>Defined based on the measurement of (s_c) of ((NH_4)_2SO_4) particles classified by the DMA that is calibrated with DMA2 (^d)</td>
<td>6–11% (2–9%) (^e)</td>
</tr>
<tr>
<td>RH in DMA2</td>
<td>0.3% (0.9%) (^f)</td>
<td>&lt; 2% (^g)</td>
<td></td>
</tr>
<tr>
<td><strong>Derived Variables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCN/CN ratio</td>
<td>2–11%</td>
<td>&lt; 10% (Estimated based on the cases of CCN/CN ~ 1.)</td>
<td>n/a</td>
</tr>
<tr>
<td>Hygroscopic growth factor (g)</td>
<td>1% (^h)</td>
<td>(\leq 2%) (Confirmed by the hygroscopic growth measurement of ((NH_4)_2SO_4) at 83% RH)</td>
<td>5% (see Fig. 2b)</td>
</tr>
</tbody>
</table>

\(^a\) One standard deviation (1SD). \(^b\) For measurements of particles whose number concentrations ranged from 0.7 to 10 particle cm\(^{-3}\), with an integration time of 3 min. \(^c\) Estimated based on the variability in the three week interval. \(^d\) From the Köhler theory section. \(^e\) Values depend on the supersaturation conditions. The widths of supersaturations including (excluding) the width of \(d_{mob,dry}\) of \((NH_4)_2SO_4\) particles classified by the DMA are presented without (with) parenthesis. \(^f\) As a result of the PID control of the humidified and dry air flows supplied to the Nafion tubes that control the RH of aerosol and sheath flows [Mochida and Kawamura, 2004]. Standard deviation of the RH reading at the inlet (outlet) of the DMA is presented without (with) parenthesis. \(^g\) Manufacturer’s warrant based on the calibration using Vaisala HMK15. The outlet RH equals to the inlet RH +0.2% on average. \(^h\) Determined from growth factor measurements for 100 nm \((NH_4)_2SO_4\) particles at 83% RH.
Table 2. Chemical compositions of aerosol particles (wt%) measured by AMS ($d_{\text{na}}$: 50–200 nm).

<table>
<thead>
<tr>
<th>Component</th>
<th>Range</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>2–23</td>
<td>7</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>&lt;1–16</td>
<td>5</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>&lt;1–6</td>
<td>2</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>2–20</td>
<td>10</td>
</tr>
<tr>
<td>Organics</td>
<td>36–65</td>
<td>54</td>
</tr>
<tr>
<td>EC $^a$</td>
<td>8–35</td>
<td>24</td>
</tr>
</tbody>
</table>

$^a$ Since AMS does not detect elemental carbon (EC), concentrations of EC were estimated from the characteristic peak of the hydrocarbons at m/z 57, which usually correlates to the amount of EC in an urban environment [Zhang et al., 2005c]. The scaling factor was determined by comparison with EC concentrations obtained by a Sunset Laboratory OC/EC analyzer.
Table 3. Sensitivity analysis of the thresholds of $B$ and $g$ to be CCN active, in the case that the set point of the supersaturation in the CCN counter is 0.22%.

<table>
<thead>
<tr>
<th>Perturbation (%) $^a$</th>
<th>$\Delta B_{\text{threshold}}$ (%)</th>
<th>$\Delta g_{\text{threshold}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta s_c = -5 / +5$</td>
<td>+10.8 / -9.3</td>
<td>+1.9 / -1.7</td>
</tr>
<tr>
<td>$\Delta RH_{\text{HTDMA}} = -0.3 / +0.3 (-0.9 / +0.9)^c$</td>
<td>n/a $^b$</td>
<td>+0.3 / -0.3 (+0.9 / -0.9) $^c$</td>
</tr>
<tr>
<td>$\Delta d_{\text{mob,dry}} = -1 / +1$</td>
<td>+3.1 / -2.9</td>
<td>+0.5 / -0.5</td>
</tr>
</tbody>
</table>

$^a$ Based on precisions in Table 1. $^b$ Not calculated because the perturbation of RH alters the relationship between $B$ and $g$ (i.e., the axes of $B$ in Figure 8 and 9). $^c$ Based on the RH reading at the outlet of DMA2.
Table 4. Correlations of fractions of organics with $N_{\text{CCN\_pred}}/N_{\text{CCN\_meas}}$.

<table>
<thead>
<tr>
<th>ratios</th>
<th>$r$</th>
<th>$P(r = 0)$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OM/(WSIM+OM)</td>
<td>-0.37</td>
<td>4.0</td>
</tr>
<tr>
<td>HOM/(WSIM+OM)</td>
<td>-0.57</td>
<td>0.08</td>
</tr>
<tr>
<td>OOM/ (WSIM+OM)</td>
<td>0.47</td>
<td>0.7</td>
</tr>
<tr>
<td>HOM/OM</td>
<td>-0.63</td>
<td>0.02</td>
</tr>
<tr>
<td>OOM/OM</td>
<td>0.63</td>
<td>0.01</td>
</tr>
</tbody>
</table>

a Number of samples is 31. The $N_{\text{CCN\_pred}}/N_{\text{CCN\_meas}}$ value is derived with the KP model. b OM: organic mass; WSIM: water soluble inorganic mass; HOM: hydrocarbon-like organic mass; OOM: oxygenated organic mass. Details of the determination of HOM and OOM from the AMS data are presented in Zhang et al. [2005b]. c Correlation coefficient. The errors in $r$ associated with systematic errors in $N_{\text{CCN\_pred}}/N_{\text{CCN\_meas}}$ (see Figure 10a) are up to 0.05. d Limit of the probability that the null hypothesis $r = 0$ is rejected.
Fig. 2  Mochida et al.

(a) Distribution of humidified particles.

(b) Hygroscopic growth factor distribution.

(c) Weighting function distribution.
Fig. 3 Mochida et al.
Fig. 4 Mochida et al.

(a) 0.22% SS
(b) 0.55% SS
(c) 0.82% SS
(d) 1.3% SS

Dry Particle Diameter $d_{\text{mob,dry}}$ (nm)
Fig. 5  Mochida et al.

RH(HTDMA) = 83%

(a) 30 nm (n=5)  
(b) 50 nm (n=4-6)  
(c) 80 nm (n=2-6)  
(d) 100 nm (n=6-37)
(e) 150 nm (n=2-5)
(f) 200 nm (n=2)

RH(HTDMA) = 89%

(g) 50 nm (n=6-7)
(h) 100 nm (n=6)

CCN/CCN Ratio  
Hygroscopic Growth Factor $g$
Fig. 7 Mochida et al.

(a) CN (normalized)

(b) CCN at 0.22% SS (normalized)

(c) CCN at 0.55% SS (normalized)

(d) Mass Fraction ($d_{v<200nm}$)

Date & Time, 2004

<table>
<thead>
<tr>
<th>Mass Fraction ($d_{v&lt;200nm}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO3</td>
</tr>
<tr>
<td>SO4</td>
</tr>
<tr>
<td>NH4</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>Org</td>
</tr>
<tr>
<td>EC</td>
</tr>
</tbody>
</table>

0.0 0.2 0.4 0.6 0.8 1.0

00:00 11/11 11/12
Fig. 8  Mochida et al.

(a) $d_{mob,dry} = 80$ nm

Threshold: 0.22% SS

(b) $d_{mob,dry} = 100$ nm

Threshold: 0.22% SS

(c) $d_{mob,dry} = 150$ nm

Threshold: 0.22% SS

Hygroscopic growth factor $g$
Fig. 9 Mochida et al.

(a) $d_{mob,dry} = 100$ nm

Threshold: 0.22% SS

25% decrease in surface tension

(b) $d_{mob,dry} = 100$ nm

Threshold: 0.22% SS
Fig. 10  Mochida et al.

(a) KP
- base case ($\Delta \sigma/\sigma = 0\%$ and $B_{83}/B_{SS}=1.0$)
- $\Delta \sigma/\sigma = -12.5\%$ (or $B_{83}/B_{SS}=0.67$)
- $\Delta \sigma/\sigma = -25\%$ (or $B_{83}/B_{SS}=0.42$)

(b) K2005
- base case ($\Delta \sigma/\sigma = 0\%$ and $B_{83}/B_{SS}=1.0$)
- $\Delta \sigma/\sigma = -12.5\%$ (or $B_{83}/B_{SS}=0.67$)
- $\Delta \sigma/\sigma = -25\%$ (or $B_{83}/B_{SS}=0.42$)