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

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\[1\] As described by the Köhler theory, the hygroscopicity of atmospheric aerosol particles is a key factor regulating their cloud condensation nuclei (CCN) activity. Here we investigated the relationship between hygroscopicity and CCN activity for urban aerosol particles 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 10 to 17 November 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 found to be 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 simultaneously measured using an aerosol mass spectrometer. They 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 nonideality of organics from inorganic salts. These factors associated with organics are potentially important for CCN activity and thus microphysical cloud processes in the atmosphere.


1. Introduction

[2] 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.

[3] 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 depress 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

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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., Shulman 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, 2002].

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 monodispersed and polydispersed aerosol particles using a HTMDA and a CCN counter in parallel [Brechlet and Kreidenweis, 2000b; 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 in Tokyo was investigated using a novel instrumental setup: a HTMDA coupled in series to a CCN counter. The HTMDA 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 HTMDA-CCNC system enabled us to measure the CCN activity of urban aerosol particles as functions of both dry particle size and hygroscopicity. Here we report for the first time the simultaneous measurements of hygroscopicity and CCN activity of atmospheric particles in series, and discuss new insights concerning the behavior of CCN and thus mechanisms for the formation and growth of cloud droplets.

2. Experimental Section

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:

\[
\ln S = \frac{2A}{d_{wet}} - \frac{Bd_{ve,dry}}{d_{wet}} = \frac{2\sigma M_w}{\rho_w RT} - B \ln \phi = \frac{2\sigma M_w}{\rho_w M_i},
\]

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 \( M_i \) are the molecular weights of water and solute, respectively, and \( \rho_w \) and \( \rho_i \) 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 Klett, 1997]. \( R \) and \( T \) are the gas constant and temperature, respectively. This equation can be extended for a multicomponent system, by modifying the hygroscopicity \( B \) in equation (1) to be

\[
B = \frac{M_w}{\rho_w} \sum_i \frac{\nu_i \phi_i \xi_i m_i}{M_i} \left/ \sum_i \frac{m_i}{\rho_i} \right.
\]

where \( \nu_i \), \( \phi_i \), \( \xi_i \), \( m_i \), \( M_i \) are the degree of dissociation, the osmotic coefficient, the degree of dissociation, 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 \( d_{wet} \) is much larger than \( d_{ve, dry} \), 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 \( d_{ve, dry} \), from

\[
\ln S_c = \frac{2}{3B} \left( \frac{2A}{3d_{ve, dry}} \right)^{3/2} = s_c,
\]

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 \( d_{ve, dry} \) 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 HTMDA-CCNC System

The experimental setup of the HTMDA-CCNC system is presented in Figure 1. In the HTMDA part, sample atmospheric aerosols (PM1) were dried in tandem diffusion dryers (TSI Model 3062) filled with silica gel and molecular sieve (13X/4A, Speleo). 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 HTMDA 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 in 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 by 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 $297.6 \pm 0.7$ (297.8 $\pm 0.7$) 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 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 ($d_{mob}$) 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 nonnegligible fractions of particles have larger diameters ($\sim \times 1.5$ 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 by Jayne et al. [2000] and Takegawa et al. [2005]. Mass concentrations of chemical components integrated over specific ranges of vacuum aerodynamic diameter ($d_{vac}$) measured by the AMS were used to represent the chemical compositions of monodisperse aerosol particles in the HTDMA-CCNC system. Since the ratio of $d_{vac}$ to electrical mobility diameter ($d_{mob}$) can be dependent on particle morphology and density [DeCarlo et al., 2004], we present here the mass concentrations at $d_{vac}$ 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 VTDMA 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 nonvolatile components (mainly elemental carbon) in the particles. The results from the instrument are presented in a separate paper (M. Kuwata et al., Cloud condensation nuclei (CCN) activity of non-volatile particles in Tokyo, submitted to Journal of Geophysical Research, 2006, hereinafter referred to as Kuwata et al., submitted manuscript, 2006).

[12] In parallel to the HTDMA-CCNC and the AMS, a Scanning Mobility Particle Sizer (SMPS, TSI Model 3034) was operated 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.

[13] The aerosol measurements using the HTDMA-CCNC system were carried out at the Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan from 10 to 17 November 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 10 to 12 November, temporal variation of hygroscopicity and CCN activity of aerosol particles were obtained semicontinuously for particles whose dry diameters were 100 nm. From 12 to 16 November, particles whose dry diameters were 30, 50, 80, 100, 150, and 200 nm were measured periodically. During the period of 10–16 November, the hygroscopicity of particles was measured at 83% RH. On 17 November, the hygroscopicity for 50 and 100 nm particles was measured at 89% RH. Only a limited number of samples were measured at 89% RH because of the limited period of the investigation.

[14] 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

[15] The hygroscopic growth factor \( g \), which can be measured using the HTDMA, is the ratio of the humidified to dry particle diameters:

\[
\frac{d_{\text{mob}}(RH)}{d_{\text{mob, dry}}} = \frac{d_{\text{ev,dry}}(RH)}{d_{\text{ev, dry}}} \tag{4}
\]

where \( d_{\text{ev,dry}} \) and \( d_{\text{ev}(RH)} \) (or \( d_{\text{mob,dry}} \) and \( d_{\text{mob}(RH)} \)) 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, \( d_{\text{mob, dry}} \) 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

\[
\ln a_w = - \frac{Bd_{\text{ev, dry}}}{d_{\text{ev, dry}}(RH)^3 - d_{\text{ev, dry}}^3} \leq - \frac{Bd_{\text{mob, dry}}}{d_{\text{mob}(RH)^3} - d_{\text{mob, dry}}^3} \tag{5}
\]

under subsaturated conditions. Equations (1), (4) and (5) give the relationship between the bulk hygroscopicity \( B \) and the hygroscopic growth factor \( g \):

\[
B = (1 - g^3) \ln a_w. \tag{6}
\]

Under subsaturated 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 \( S \), because of the surface tension effect (Kelvin effect) of particles. The relationship between \( S \) and \( a_w \) is given from equations (1) and (5) by:

\[
S(\equiv RH\%/100) = a_w \exp\left( \frac{2A}{d_{\text{ev}}(RH)} \right) \tag{7}
\]

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 \((NH_4)_2SO_4\) and \(NH_4NO_3\) 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 later.

2.4. Derivation of the CCN Distribution as a Function of Hygroscopicity

[16] Particle number (CN) distributions as a function of hygroscopic growth factor \( g \) were obtained by scanning DMA2 and by recording the number of particles exiting from DMA2, with a size resolution of 64 channels/digit (Figure 2a). On the basis of the CN distribution, the distribution of CCN was obtained as follows. CCN numbers were measured at four different hygroscopic growth factors: 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, \( k(g) (j = 1, 2, 3 \text{ and } 4) \), were estimated from the experimentally derived transfer function of the first and second DMAs (Figure 2b); the monodisperse size distribution of \((NH_4)_2SO_4\) particles processed in the HTDMA under dry conditions \((d_{\text{mob, dry}} = 30–200 \text{ nm}) \) was measured using DMA2 and the CN counter as SMPS, and was approximated to be the transfer functions for the atmospheric particles with the same \( d_{\text{mob, dry}} \). 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 \( w_j(g) (j = 1, 2, 3 \text{ and } 4) \) presented in Figure 2c are derived from \( k_j(g) \) by the equation:

\[
    w_j(g) = k_j(g) / \sum k_j(g),
\]

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

\[
    \frac{dy_{CCN}(g)}{d \log g} = \frac{dy_{CN}(g)}{d \log g} \sum_{j=1}^4 w_j(g) r_j,
\]

where \( r_j \) is the CCN/CN ratio at four set points of hygroscopic growth factors \( g \), and \( y_{CN}(g)/d \log g \) and \( y_{CCN}(g)/d \log g \) 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/CN ratio was estimated to be less than 10%.

The classification of DMA1 and DMA2 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 \((NH_4)_2SO_4\) particles with one DMA and by measuring the mode diameter with the other. The same procedure was performed between DMA2 and another DMA (DMA3) 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 DMA1 and DMA2 were 1%. The width of \( d_{mob} \) 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., \( d_{ce} = d_{mob} \)) are discussed in section 6.3.

Figure 2. (a) An example of the measured distributions of CN (unshaded histogram) and CCN (shaded histogram) numbers as a function of hygroscopic growth factor \( g \). Solid circles show hygroscopic growth factors at which CCN numbers were measured. (b) 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.
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. Supersaturation conditions are presented on the basis of the calibration using the (NH₄)₂SO₄, on the assumption of Köhler curves at T = 308 K, and φ calculated from the Pitzer equation [Pitzer and Mayorga, 1976], hereinafter referred to as KP. The droplet surface tension of (NH₄)₂SO₄ in this calculation is based on the relationship given by Hänel [1976].

As presented by 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, hereinafter 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 by Kreidenweis et al. [2005]. Because K2005 is based on a parameterization at 298 K, a correction factor of 0.952 (= (298/308)⁰.⁵) derived from equations (1) and (3) was applied to determine Sₑ at 308 K. Note that the standard Köhler model with φ = 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 ≤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 (≤2%) leads to ≤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].

Table 1. Random and Systematic Errors and Width of the Variables in the HTDMA-CCNC Experiment

<table>
<thead>
<tr>
<th>Variables</th>
<th>Random Error* (Precision)</th>
<th>Systematic Error (Trueness)</th>
<th>Width*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured variables</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN count</td>
<td>1–4%</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>CCN count</td>
<td>2–10%</td>
<td>calibrated with DMA2</td>
<td>4%</td>
</tr>
<tr>
<td>dₘmob classified by DMA1</td>
<td>1%</td>
<td>calibrated using DMA</td>
<td>4%</td>
</tr>
<tr>
<td>dₘmob classified by DMA2</td>
<td>1%</td>
<td>used as a reference DMA, calibrated using PSL particles</td>
<td></td>
</tr>
<tr>
<td>Supersaturation</td>
<td>5%</td>
<td>defined on the basis of the measurement of sₑ of (NH₄)₂SO₄ particles classified by the DMA that is calibrated with DMA2</td>
<td>6–11% (2–9)%</td>
</tr>
<tr>
<td>RH in DMA2</td>
<td>0.3% (0.9)%</td>
<td></td>
<td>n/a</td>
</tr>
<tr>
<td>Derived variables</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCN/CN ratio</td>
<td>2–11%</td>
<td>&lt;2%≈#</td>
<td></td>
</tr>
<tr>
<td>Hygroscopic growth factor g</td>
<td>1%</td>
<td>&lt;2% (confirmed by the hygroscopic growth measurement of (NH₄)₂SO₄ at 83% RH)</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*One standard deviation (1SD).
#For measurements of particles whose number concentrations ranged from 0.7 to 10 particle cm⁻³, with an integration time of 3 min.
##Estimated on the basis of the variability in the three week interval.
###From the Köhler theory combined with the Pitzer model (KP). Application of other CCN activation models is discussed in sections 6 and 7.
####Values depend on the supersaturation conditions. The widths of supersaturations including (excluding) the width of dₘmob,h of (NH₄)₂SO₄ particles classified by the DMA are presented without (with) parenthesis.
#####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.
######Manufacturer’s warrant based on the calibration using Vaisala HMK15. The outlet RH equals to the inlet RH +0.2% on average.
#####Determined from growth factor measurements for 100 nm (NH₄)₂SO₄ particles at 83% RH.

[20] 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. Supersaturation conditions are presented on the basis of the calibration using the (NH₄)₂SO₄, on the assumption of Köhler curves at T = 308 K, and φ calculated from the Pitzer equation [Pitzer and Mayorga, 1976], hereinafter referred to as KP. The droplet surface tension of (NH₄)₂SO₄ in this calculation is based on the relationship given by Hänel [1976].

[21] As presented by 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, hereinafter 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 by Kreidenweis et al. [2005]. Because K2005 is based on a parameterization at 298 K, a correction factor of 0.952 (= (298/308)⁰.⁵) derived from equations (1) and (3) was applied to determine Sₑ at 308 K. Note that the standard Köhler model with φ = 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.

[22] The systematic error of RH measurement in the HTDMA is ≤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 (≤2%) leads to ≤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].

[23] The hygroscopic growth factor g of pure (NH₄)₂SO₄ particles at 83% RH in DMA2 were measured (n = 2) during the field campaign. The measured values 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 campaign.

[24] A possible difference in hygroscopicity under supersaturation conditions at 308 K (B₈₃) and those at 83% and 89% RH, 298 K (B₈₃ and B₈₉) is critical for the interpretation of HTDMA-CCNC data. If major inorganic salts in sample atmospheric aerosols remain as solids after they are
Table 2. Chemical Compositions of Aerosol Particles (wt %)
Measured by AMS (dca: 50–200 nm)

<table>
<thead>
<tr>
<th>Component</th>
<th>Range</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO3⁻</td>
<td>2–23</td>
<td>7</td>
</tr>
<tr>
<td>SO4²⁻</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>NH4⁺</td>
<td>2–20</td>
<td>10</td>
</tr>
<tr>
<td>Organics</td>
<td>36–65</td>
<td>54</td>
</tr>
<tr>
<td>EC</td>
<td>8–35</td>
<td>24</td>
</tr>
</tbody>
</table>

*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.

humidified in the HTDMA, then this leads to a large difference between $R_{33}$ (or $R_{88}$) and $R_{88}$ by change of $\varepsilon$ in equation (2). However, we conclude that this is very unlikely under our experimental conditions, on the basis of the following results. First, when pure (NH$_4$)$_2$SO$_4$ particles of 30–200 nm 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 (NH$_4$)$_2$SO$_4$ does deliquescence under our experimental conditions. This result is consistent with another HTDMA study [Hämmeri et al., 2000]. Second, since other possible major components of inorganic salts, such as NH$_2$NO$_3$, NH$_4$Cl, NH$_4$HSO$_4$, (NH$_4$)$_2$H(SO$_4$)$_2$, have lower bulk deliquescence RH than (NH$_4$)$_2$SO$_4$, these fractions in atmospheric particles may also deliquesc in the HTDMA system. Third, these inorganic salts are mixed with organics in the atmosphere, and several laboratory studies show evidence that they deliquesce at lower RH than pure salts [e.g., Parsons et al., 2004].

[25] Other factors that potentially alter $\beta$ as a function of RH are discussed later. They include a change in the osmotic coefficient $\phi$ of inorganic salts, and changes in $\nu \phi$ and $\varepsilon$ of organic compounds.

[26] 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 $d_{\text{mob}}$ was observed. This implies that, at least between DMA1 and DMA2, evaporation/condensation of semivolatile 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.

[27] 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 timescale of hygroscopic growth is longer than 2–3 s is only <2% for 50 and 100 nm particles [Chuang, 2003].

3. General Characteristic of the Atmospheric Aerosol Conditions

3.1. Chemical Compositions

[28] Table 2 summarizes the means and ranges of the relative abundances of major chemical species that were obtained by the AMS for particles whose $d_{\text{ca}}$ ranged from 50 to 200 nm. Organics is the dominant class of compounds (mean: 54%, Table 2). Such high abundances of organics were also observed in previous AMS studies in Tokyo [Takegawa et al., 2006], where it is interpreted by a large contribution of motor vehicular emissions. The AMS spectra indicate the presence of both hydrocarbon-like and oxygenated organics (see section 8); the former is mainly primary in origin whereas the latter is secondary [Zhang et al., 2005a, 2005b, Takegawa et al., 2006] and water-soluble [Kondo et al., 2006]. 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.

3.2. Hygroscopic Growth Factor

[29] 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 monodispersed particles ($d_{\text{mob,dry}} = 100$ nm) by the addition of water vapor leads

![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. Hygroscopicity $B$ is shown at the top of the figure.](image-url)
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 \cite{Heintzenberg2001, Gasparini2004}. The deviation of the distribution presented as the shaded area suggests that the relative abundance of particles on certain hygroscopic modes varied substantially depending on time during the campaign.

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, suggesting that they 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 hygroscopicity corresponded to that of pure (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ was negligibly small. On the basis of 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.

3.3. CCN Size Distribution

Figure 4 presents examples of CN and CCN size distributions averaged from 14 to 15 November at 0.22, 0.55, 0.82, and 1.3% supersaturations. Size distributions averaged from 2300 LT, 14 November to 2100 LT, 15 November 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 the 0.22% supersaturation, the CCN/CN ratio was extrapolated toward larger diameters on the assumption that the CCN/CN ratio is unity for 300 nm particles.

Figure 5. 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 30 (Figure 5a), 50 (Figures 5b and 5g), 80 (Figure 5c), 100 (Figures 5d and 5h), 150 (Figure 5e) and 200 (Figure 5f) 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 5

RH(HTDMA) = 83%

- O- 0.22% SS  ▲ 0.55% SS  - □- 0.82% SS  - ■ 1.3% SS

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

Hygroscopic growth factor $g$

Figure 5
0.55, 0.82 and 1.3% supersaturation. The range of dry diameters classified by DMA1 in this study (30–200 nm) cover the dominant particle size ranges of CCN. While the CCN/CN ratio starts to decrease toward the smaller particle diameter below $d_{\text{mob,dry}} = 200$ 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).

4. CCN/CN Ratios for Particles With Different Hygroscopicity

[32] Using the HTDMA-CCNC system, the CCN/CN ratios were obtained for four different hygroscopic growth factors (or hygroscopicity) 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 supersonsation, hygroscopicity, and dry particle diameters. For instance, for 30 nm particles at 83% RH (Figure 5a), significant numbers of CCN were observed only at the highest supersaturation of 1.3%, and hygroscopicity of 1.24 and 1.38. In the case of 50 nm particles (Figure 5b), the CCN/CN ratios are clearly different from those of 30 nm particles; more CCN was observed for each hygroscopicity and supersaturation. For the particle diameters $\geq 80$ nm, the CCN/CN ratios were almost unity at hygroscopic growth factor $g \geq 1.11$ except at 0.22% supersaturation. 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%).

[33] In general, larger particles are more CCN active than smaller particles (Figures 5a–5e). 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. 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).

[34] Limited numbers of data were also collected under the condition of 89% RH in the HTDMA (Figures 5g and 5h). The results indicate that the spectra of the CCN/CN ratios versus hygroscopic growth factor for various supersaturation 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 $B$ show larger hygroscopic growth factor $g$ at higher RH in the HTDMA.

5. Time Series of the CCN Distribution as a Function of Hygroscopicity

[35] On the basis of the method described in the experimental section, semicontinuous distributions of CCN numbers as a function of hygroscopic growth factor $g$ were calculated. Figures 6a–6c present temporal variations of the CN and CCN distributions as a function of $g$ for 100 nm particles on 10–12 November. The $z$ axis unit is $dN$ (particle cm$^{-3}$)d$g$, 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 $< d_{\text{ca}} <$ 200 nm) are also presented in Figure 6d, as estimates of the compositions of particles at $d_{\text{mob,dry}} = 100$ nm.

[36] 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 2200 LT, 10 November to 1200 LT, 11 November and 0300–1900 LT, 12 November 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 11 November (Figure 6a) is coincident with the increase in the mass of SO$_2^-$ 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 nonrefractory components, whereas less-hygroscopic particles are mainly composed of nonvolatile components (Kuwata et al., submitted manuscript, 2006). As explained in section 3.2, 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$_3$ ($g \sim 1.5$), 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 2300 LT, 10 November to 0700 LT, 11 November, a fraction of the particles whose hygroscopic growth is intermediate (1.1–1.2) increased, suggesting that the organic fraction became substantial during the period.

[37] Number distributions of CCN, instead of CN, as a function of hygroscopic growth factor $g$, provide novel data sets 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 4 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 11 November) 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 demonstrate an importance of hygroscopicity for the variation of CCN numbers in the atmosphere.

[38] The data shown in Figures 6a–6d are also presented in Figures 7a–7d 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 a basis of normalized distribution, the CN and CCN fractions at around $g = 1.4$ from 1100 LT, 11 November to 0100 LT, 12 November were significant (Figures 7a–7c), being consistent with the increase in SO$_4^{2-}$ mass fraction shown in Figure 7d.

6. CCN Activity as a Function of Particle Hygroscopicity

[39] The CCN number distributions as a function of hygroscopicity are subjected to the model assessment using equations (1)–(3), to evaluate the influence of the hygroscopicity measured by the HTDMA on 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.

[40] Among the obtained data sets, we have found that the degree of agreement between the models and the measurements is substantially different from sample to sample. First we present the 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 6.1). 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 6.2). Possible errors associated with particle morphology (section 6.3) and nonconstant surface tension and hygroscopicity under supersaturation conditions (section 6.4) 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 experimental observations.

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 ($d_{av}: 50–200$ nm).
on the theoretical relationship between hygroscopic growth factor $g$, hygroscopicity $B$, and critical supersaturation $s_c$.

### 6.1. Case 1: Good Prediction of the CCN Activity by the Base Model

[41] Figures 8a–8c present number distributions of both aerosol particles (CN) and CCN as a function of hygroscopic growth factor on 14 November 2004. Particles of dry diameters at 80, 100 and 150 nm were humidified to 83% in the HTDMA, and CCN at 0.22% supersaturation is presented here. 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 according to equations (1)–(3). Further, equations (5) and (6) give the hygroscopic growth factor $g$ corresponding to the thresholds of $B$. In Figures 8a–8c, the thresholds of $B$ and $g$ calculated are presented as vertical thick lines. The ranges of systematic errors, associated with RH ($\pm 2\%$), 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 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 $B_{83}/B_{ss}$-RH relationships of ($NH_4)_2SO_4$ and $NH_4NO_3$ 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 $A = 1.0 \times 10^{-3}$ m at 308 K. This is reasonable for most inorganic particles [Brechtel and Kreidenweis, 2000a], whereas it is possibly not correct for some organic/inorganic mixtures [Shulman et al., 1996; Facchini et al., 1999]. The third assumption is the determination of supersaturation in the CCN counter by the KP model.

[42] Taking into account the width of supersaturation RH in the CCN counter, we further estimated the nonstepwise change in the CCN/CN ratios around the threshold of $B$. Widths of supersaturation without correction of the size widths of ($NH_4)_2SO_4$ 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–8c. The error bars represent random errors in the predicted CCN distribution (see section 6.2), 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

**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 ($d_{sc}$: 50–200 nm).
approach in this study. Because the main component of these nonhygroscopic particles is estimated to be elemental carbon, they are probably aggregates and have nonspherical 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 nonspherical crystals; (2) even liquid ammonium sulfate particles dried \((d_{\text{mob}} < 200 \text{ nm})\) 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 [McMurry et al., 1996]. The validity of this assumption is further discussed in section 6.3.

The good agreement between the predicted and measured CCN distributions as a function of \(g\) shows that the introduction of surface tension reduction [Facchini et al., 1999] is not necessary for explaining the data presented in Figure 8. Furthermore, \(B_{83}\) is nearly equal to \(B_{\text{ss}}\), 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 \(B_{83}/B_{\text{ss}}\) for pure \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NH}_4\text{NO}_3\) 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 nonideal behavior.

With the application of the some other CCN activation models [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, \(B_{83}/B_{\text{ss}}\) 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 [Facchini et al., 1999]. Moreover, it is difficult to reasonably explain \(B_{83}/B_{\text{ss}}\) being significantly larger than unity, because both the dissolution/dissociation of organics by dilution, and the presence of \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NH}_4\text{NO}_3\) lower the \(B_{83}/B_{\text{ss}}\) 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 \((\text{NH}_4)_2\text{SO}_4\) 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 reequilibration 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 and a value of significantly larger than unity. Results from K2005 are also discussed to assess the potential uncertainty of the discussion.

6.2. Case 2: Presence of Unpredicted CCN Fraction

[46] In contrast to the results shown in Figures 8a–8c, the numbers of CCN larger than that predicted by the assumptions above (i.e., application of KP to determine the supersaturation RH, , and 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, 1998] 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).

[47] Temporal variation of supersaturation (random error: 5%) may in part be responsible for the deviation of the threshold of , 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 and in the case that the set point of supersaturation is 0.22%. It is shown that the possible random errors in the thresholds of and are mainly associated with the random error in , and those from other factors, RH and , (which relate to the precision of in Table 2), are minor. Change in the threshold of as a result of changes in from +1 to −1 SD is 20% (={+10.8% − (−9.3%)}, whereas the difference in the threshold of required to explain Figures 8 and 9 are 50%, which corresponds to 5 SD change of .

[48] A likely explanation for the discrepancy between the measured and predicted CCN distributions is that either or both of the assumptions of , and are not appropriate in the case presented in Figure 9a. First, if we assume that hygroscopicity measured using HTDMA is not largely different from that under the supersaturation condition (), 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 values in Table 2). Facchini et al. [1999] have suggested on the basis of 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 and to be CCN active (Figure 9b).

Table 3. Sensitivity Analysis of the Thresholds of and 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>ΔB_{threshold}, %</th>
<th>Δg_{threshold}, %</th>
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<tbody>
<tr>
<td>Δs_{mob,dry} = -5/5</td>
<td>+10.8/−9.3</td>
<td>+1.9/−1.7</td>
</tr>
<tr>
<td>ΔRH_{HTDMA} = -0.3/0.3</td>
<td>n/a</td>
<td>+0.3/−0.3</td>
</tr>
<tr>
<td>ΔRH_{HEDG} = (-0.9/0.9)</td>
<td>ΔB_{threshold} = -1/1</td>
<td>+3.1/−2.9</td>
</tr>
<tr>
<td>ΔRH_{HTDMA} = 0.9/−0.9</td>
<td>Δg_{threshold} = 0.5/−0.5</td>
<td></td>
</tr>
</tbody>
</table>

aBased on precisions in Table 1.

bNot calculated because the perturbation of RH alters the relationship between and (i.e., the axes of in Figures 8 and 9).

cBased on the RH reading at the outlet of DMA2.

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 10 November 2004. Predicted CCN distributions by assuming (a) \(\Delta \sigma/\sigma = 0\) % and (b) \(\Delta \sigma/\sigma = -25\)% were superimposed as (a) blue (Figure 9a) and green (Figure 9b) 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 the range of the systematic error, respectively. Hygroscopicity \(B\) and the possible change of the threshold \(B\) and the threshold of hygroscopicity \(B\) to be CCN active (Figure 9b).
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 on the basis of a constant σ 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 6.4.

The difference in hygroscopicity B under subsaturated and supersaturated conditions (i.e., \( B_{32}/B_{ss} \neq 0 \)) 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 \( B_{32}/B_{ss} = 0.42 \). Such difference in the hygroscopicity B could be caused by the RH dependence of the nonideality term \( \nu / \phi \) and the degree of dissolution \( \varepsilon \) [Shulman et al., 1996]. If the particle is assumed to be composed of an insoluble core and an \((NH_4)_2SO_4 \) or \( NH_4NO_3 \) 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). Note that the \( B_{32}/B_{ss} \) ratios for \((NH_4)_2SO_4 \) and \( NH_4NO_3 \) in the core-shell models are 0.81 and 0.66, respectively, which are close to those for pure \( (NH_4)_2SO_4 (0.79) \) and \( NH_4NO_3 (0.66) \). In addition, if only inorganic salts generally govern \( B_{32}/B_{ss} \) 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 \( B_{32}/B_{ss} \) 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 \( B_{32}/B_{ss} \) ratio. They may also relate to the variation of the ratio, in addition to that originating from \( \Delta \xi \) (Table 3). If the nonideality 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 \( B_{32}/B_{ss} \). Furthermore, temporal variation of characteristics of organics, e.g., the degree of oxidation, may also change \( B_{32}/B_{ss} \) 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 this study.

6.3. 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 nonspherical, the volume equivalent diameter \( d_{ve} \) is smaller than the mobility diameter \( d_{mob} \). Given that dry particles of more-hygroscopic mode are nonspherical 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 subsaturated 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 \( s_c \). [52] 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 nonspherical 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 \( \chi_d \) less than 1.04 for \( d_{mob} < 200 \) nm, and that addition of organics to ammonium sulfate particles further lowers \( \chi_d \) [Zelenyuk et al., 2006]. We hereby 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 \( \chi_c \) 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.

6.4. Changes in Surface Tension and Hygroscopicity in Supersaturation Conditions

In section 6.2, negative \( \Delta \sigma / \sigma \) values and \( B_{32}/B_{ss} \) 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 nonconstant 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
from equation (3) to be 0.14%. Next we calculated $s_c$ numerically, applying $\Delta \sigma/\sigma$ as a function of $d_{\text{mob}}(\text{RH})$ [Facchini et al., 1999]. The WSOC fraction in particles was adjusted so that the same critical supersaturation condition (0.14%) was established without changing $d_{\text{mob, dry}}$, $B_{SS}$ 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 $\sigma - d_{\text{mob}}(\text{RH})$ 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 $\sigma = f(d_{\text{mob}}(\text{RH}))$ near the supersaturation condition is larger.

[55] Similar to the case of nonconstant 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 $B_{SS}/B_{83}$ 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 $B - d_{\text{mob}}(\text{RH})$ relationship.

### 7. Measured Versus Predicted CCN Numbers

[56] 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 on the basis of 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 $B_{SS}/B_{83} = 1$. They are equivalent to the assumptions that $B_{SS}/B_{83}$ are 1, 0.67 and 0.42 in the case $\Delta \sigma/\sigma = 0$. In Figure 10a (KP), most of the data points for the assumptions $\Delta \sigma/\sigma = 0$ and $B_{SS}/B_{83}$ are 1 are between the 1:1 and 1:2 lines, indicating that this base case underpredicts the CCN numbers. The average of the ratios of predicted for the measured CCN numbers ($N_{\text{CCN,pred}}/N_{\text{CCN,meas}}$) in the base case is 0.59 (ISD: 0.24). The predicted CCN numbers on the assumption that $\Delta \sigma/\sigma = -25\%$ (or $B_{SS}/B_{83} = 0.42$) are between the 1:1 and 2:1 lines. In this case, the average of $N_{\text{CCN,pred}}/N_{\text{CCN,meas}}$ is 1.68 (ISD: 0.57).

[57] In the case of K2005 (Figure 10b), CCN numbers are overpredicted for many of the samples. In the base case ($\Delta \sigma/\sigma = 0$, $B_{SS}/B_{83} = 1$), many of the data points are between the 1:1 and 2:1 lines. The reduction of surface...
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 implies 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.

8. Chemical Compositions and the CCN Activity

[60] 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 \( N_{CCN,\text{pred}}/N_{CCN,\text{meas}} \) from its average is not sensitive to the applied model (KP or K2005). Here we present a preliminary assessment of the relationship between \( N_{CCN,\text{pred}}/N_{CCN,\text{meas}} \) and chemical compositions of more-hygroscopic mode particles estimated from the AMS data. We assume that chemical components other than EC in Table 2 are more enriched 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., submitted manuscript, 2006). In this analysis, organic components are subdivided into hydrocarbon-like and oxygenated organics according to the analytical procedure of the AMS data in the work by Zhang et al. [2005b].

[61] Table 4 presents correlations of \( N_{CCN,\text{pred}}/N_{CCN,\text{meas}} \) with ratios of different chemical components. All of the correlations presented in Table 4 are statistically significant. In particular, the correlation between \( N_{CCN,\text{pred}}/N_{CCN,\text{meas}} \) 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 \( N_{CCN,\text{pred}}/N_{CCN,\text{meas}} \) and chemical composition supports the interpretation that the observed variation of the \( N_{CCN,\text{pred}}/N_{CCN,\text{meas}} \) ratio is not merely random noise caused by fluctuations of \( s_c \) and other variables.

[62] The correlation between HOM/OM (or OOM/OM) and \( N_{CCN,\text{pred}}/N_{CCN,\text{meas}} \) indicates that the underprediction of the CCN numbers is 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 6 and 7). 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.

9. Comparison With Previous CCN Studies and Future Perspectives

[65] As explained in the introduction section, hygroscopicity and CCN activity of atmospheric aerosol particles have been measured simultaneously in several field studies [Brechet and Kreidenweis, 2000a; Zhou et al., 2001; Dusek et al., 2003; Roberts et al., 2002; Rissler et al., 2004]. 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 HTDMA 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. Unlike previous studies, we investigated CCN activity of particles with specific size and hygroscopicity.

[64] As discussed in this paper, 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 nonideality 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 nonideality 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 subsaturated and supersaturated conditions depends on the solute compounds. Therefore it is possible that the nonideal 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.

[65] A novel approach to evaluate the relationship between hygroscopicity at subsaturated 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.

[65] 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, 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.

10. Summary

[64] 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.

[68] 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 critical 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

<table>
<thead>
<tr>
<th>Table 4. Correlations of Fractions of Organics With $N_{\text{CCN_pred}}/N_{\text{CCN_meas}}$</th>
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<tbody>
<tr>
<td>Ratios$^a$</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>OOM/(WSIM + OM)</td>
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<tr>
<td>HOM/(WSIM + OM)</td>
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<td>OOM/(WSIM + OM)</td>
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<td>HOM/OM</td>
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$^a$Number of samples is 31. The $N_{\text{CCN\_pred}}/N_{\text{CCN\_meas}}$ value is derived with the KP model.

$^b$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.

$^c$Limit of the probability that the null hypothesis $r = 0$ is rejected.
evaluated on the basis of 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. Although the estimate 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 nonideality between organics and inorganic salts. These factors associated with organics potentially contribute to the CCN activity of urban aerosol particles.

[60] 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 variations of the ratios of the predicted to measured CCN numbers are not noise, and that the composition of organics is responsible for the variations.

[70] 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 HTDMA-CCNC system may contribute to extending our knowledge of the relationship among chemical composition, hygroscopicity and CCN activity of atmospheric aerosol particles.

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