Dependence of CCN activity of less volatile particles on the amount of coating observed in Tokyo

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[1] A novel observation system has been developed to measure cloud condensation nuclei (CCN) activity simultaneously with volatility of aerosol particles at 400°C. CCN/CN ratios were measured using a CCN counter and a condensation particle counter, and volatility was measured with a volatility tandem differential mobility analyzer (VTDMA). This system was connected to a hygroscopicity tandem differential mobility analyzer in tandem to measure these properties of hygroscopicity-selected particles. These instruments were deployed in Tokyo in November 2004. In Tokyo, the dominant fraction of nonvolatile cores at 400°C has been found to be black carbon (BC). Therefore the number size distribution measured by VTDMA represents the mixing state of black carbon particles. The VTDMA measurement of hygroscopicity-selected particles revealed that most of the less hygroscopic particles were less volatile, while more hygroscopic particles were more volatile. CCN/CN ratios of less volatile particles [(CCN/CN)_{LV}] are estimated from CCN activity and volatility measurements of less hygroscopic particles. (CCN/CN)_{LV} at SS = 0.5% is correlated with the decrease of peak diameter due to volatilization (Δdn), and (CCN/CN)_{LV} is nearly equal to unity at Δdn = 10 nm. This result suggests that the CCN activity of BC particles significantly depends on the amount of coating.


1. Introduction

[2] Black carbon (BC) is emitted to the atmosphere by incomplete combustion of fossil fuels and biomass. BC strongly absorbs solar radiation, leading to radiative heating of the atmosphere [Haywood et al., 1997; Myhre et al., 1998; Jacobson, 2001, 2002; Ramaswamy et al., 2001]. It can also contribute to radiative forcing by changing snow and ice albedos [Hansen and Nazarenko, 2004]. Concentrations of BC are controlled by their transport and removal processes as well as emissions.

[3] Removal of BC is dominated by wet deposition [e.g., Jacobson, 2004]. BC particles are hydrophobic and insoluble to water soon after emission because of their graphitic structure. However, it has been shown that BC becomes hydrophilic by surface oxidation [e.g., Zubri et al., 2005] and becomes hygroscopic by condensation of secondary aerosol components [e.g., Saathoff et al., 2003; Sellegri et al., 2003]. Coated BC particles likely act as cloud condensation nuclei (CCN) although this point has not been clearly demonstrated by field measurements.

[4] Global distributions of BC have been calculated by three-dimensional models, which incorporate emissions, transport, and removal of BC [Cooke and Wilson, 1996; Chung and Seinfeld, 2005; Park et al., 2005]. One of the largest uncertainties in the model calculations is the estimate of the lifetime of BC. Almost all BC particles are assumed to be hydrophobic upon emission and become hydrophilic by the condensation of secondary aerosol compounds. The timescale of the evolution of BC properties is often given empirically in the form of an e-folding time although the timescale can vary spatially and temporally [Park et al., 2005]. For more accurate estimates of the removal rate of BC, we need to improve our understanding of the coating process of BC and the dependence of its CCN activity on the state of coating.

[5] It is advantageous to measure the aging of BC near its source regions considering the anticipated relatively short timescales for the conversion of BC properties [Saathoff et al., 2003; Park et al., 2005]. In this study, relationships between CCN/CN ratio (CCN activity) and volatility at 400°C were investigated by deploying a CCN counter [Robert and Nenes, 2005] and a volatility tandem differential mobility analyzer (VTDMA) [Clarke et al., 2004; Philippin et al., 2004] in Tokyo. Kondo et al. [2006] have shown that nonvolatile particles at 400°C are nearly equivalent to BC in Tokyo. Therefore we can study the mixing states of BC particles using VTDMA. These measurements were performed for particles selected by a hygroscopicity...
Figure 1. Relationships between the size of insoluble cores and critical supersaturations (critical SSs). The calculation was performed for particles with a dry diameter of 100 nm. The solid line shows the critical SSs of particles composed of ammonium sulfate (coating material) and an insoluble core. The critical SSs of particles coated by glutaric acid are shown as the dashed line. The volume fraction of insoluble cores ($V_{\text{core}}$) is also shown in this figure. In the region where the core diameter is larger than 80 nm, critical supersaturation strongly depends on core size. In the other region (core diameter < 80 nm) critical supersaturation is controlled by the solute composition.

3. Instruments

[8] Figure 2a shows the experimental setup used in this study (HTDMA-CCNC/VTDMA system). In this system, size and mixing state (hygroscopicity) of aerosol particles were selected by HTDMA before the measurement of CCN activity and volatility. The HTDMA part of this system is described in detail by Mochida et al., [2006]. Therefore only a brief description of HTDMA part is given here. Ambient particles were dried to a relative humidity (RH) < 4% by a diffusion dryer. The polydisperse dry particles in the sampled air were charged by a Am bipolar charger, then their size was selected by a differential mobility analyzer (DMA1; TSI Model 3081). In this study, the sheath flow to sample flow ratio of all DMAs was set at 10:1. Observation results of 100-nm particles were analyzed in this study because the number concentration of CCN is highest at 90–140 nm during the observation period [Mochida et al., 2006]. Classified particles were humified to grow into larger particles depending on their hygroscopic-

<table>
<thead>
<tr>
<th>Compound</th>
<th>$d_{\text{core}} = 0$ nm</th>
<th>20 nm</th>
<th>40 nm</th>
<th>60 nm</th>
<th>80 nm</th>
<th>100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.15</td>
<td>0.19</td>
<td>2.1</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.14</td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>0.22</td>
<td>0.22</td>
<td>0.23</td>
<td>0.25</td>
<td>0.31</td>
<td>2.1</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>0.26</td>
<td>0.26</td>
<td>0.27</td>
<td>0.30</td>
<td>0.37</td>
<td>2.1</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>0.27</td>
<td>0.27</td>
<td>0.28</td>
<td>0.31</td>
<td>0.39</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*d_{core} is the diameter of the insoluble core. SS reported in percent.
icity. The sheath flow of DMA2 was also humidified. The RH in the humidifier and DMA2 were set at 83 or 89% for the present study. The precision of RH was 0.3%. The hygroscopic growth factor, denoted as $g(RH)$, is defined as

$$g(RH) = \frac{d_p(RH)}{d_{dry}(2)}$$

where $d_p(RH)$ is the particle diameter at a given RH.

[10] The voltages applied to DMA2 were fixed to constant values to select particles with the corresponding $g(RH)$ values. This voltage was scanned once per hour to measure the number distribution of $g(RH)$. The humidified air was dried again by a Nafion dryer mounted downstream of DMA2. Then, classified dry particles were introduced to a CPC1 (TSI model 3022A), a CCN counter (CCNC, Droplet Measurement Technologies) [Roberts and Nenes, 2005], and a heater. The total number concentration of the monodisperse particle (condensation nuclei; CN) was measured by CPC1, and the CCN number concentrations were measured by the CCNC. The sample flow rate and the sheath flow rate of CCNC were set to 0.05 and 0.45 l/min, respectively. The temperature gradient ($\Delta T$) of the thermal gradient chamber in the CCNC was periodically cycled at four different values (3.6, 7.2, 10.8, and 16.2 K) for the measurements at different SS in the chamber. The SS corresponding to these $\Delta T$ values were calibrated by using dried ammonium sulfate ($\left[\text{NH}_4\right]_2\text{SO}_4$) particles. These particles were generated from an aqueous solution of ammonium sulfate by using an atomizer (TSI Model 3076). These particles were dried by a diffusion dryer, and the size was selected by a DMA. Then, they were measured by a CPC and the CCNC to obtain the distributions of CCN/CN ratios. A sigmoid function [equation (3)] was fitted to the experimental result,

$$\frac{\text{CCN}}{\text{CN}} = a + \frac{b}{1 + \exp\left(\frac{d_c - d_p}{c}\right)}$$

where $a$, $b$, and $c$ are constants obtained by fitting, and $d_c$ is the center diameter of the sigmoid function. $d_c$ was assumed as the critical dry diameter of ammonium sulfate under the observation conditions. Note that the CCN/CN ratio is not necessarily 0.5 at $d_c$ because of the existence of multiply charged particles and particle loss in the CCNC. In this study, CCN/CN ranged from 0.44 ($\Delta T = 16.2$ K) to 0.55 ($\Delta T = 3.6$ K) at $d_c$. The critical SS corresponding to the observed activation diameter was calculated by the Köhler theory at a temperature of 308 K. In this calculation, the osmotic coefficient of the aqueous solution was calculated by the Pitzer equation [Pitzer and Mayorga, 1973] as described by Mochida et al. [2006]. This SS was assumed to be equal to the SS in the CCNC. $d_c$ and the SS corresponding to each $\Delta T$ are summarized in Table 2. The precisions of the CCN and CN number concentrations were estimated to be 2–10 and 1–4% from their temporal variation, respectively. Therefore the precision of CCN/CN ratios was calculated to be 2–11%. The CCN/CN ratio for ammonium sulfate at 80 nm was 1.01. Therefore the systematic error in the CCN/CN measurement at 100 nm was negligible.

[11] The VTDMA consisted of a heater, two DMAs (TSI Model 3081), and a CPC (TSI Model 3022A). The VTDMA measures size distributions of nonvolatile cores of the size-selected particles. The sample air was heated at 400°C by a mantle heater wrapped around a stainless steel tube (3/8-inch outer diameter, 7-mm inner diameter, and 21 cm long). A thermocouple was attached to the outer wall at the center of the heated section. A proportional-integral-derivative (PID) controller (CAL3200, CAL controls) was used to maintain the temperature of the heater at 400±1°C. The average residence time of the sample air through the heated section was estimated to be 1.6 s at room temperature at the sample flow rate of 0.3 l/min. Particles with diameters prescribed by DMA1 lost their volatile components in the heated section. The size distributions of residual nonvolatile cores were measured by the DMA3-CPC2 system.

Figure 2. a) HTDMA-CCNC/VTDMA system used in this study. b) The experimental setup used for the inspection of re-condensation of the heater.
The transport efficiency of particles through the heater is one of the important heater parameters. It was measured using sodium chloride (NaCl) particles because they do not evaporate at 400°C [Brooks et al., 2002; Philippin et al., 2004]. Polydisperse NaCl particles were generated by an atomizer, were dried by a diffusion dryer, and were size-selected by a DMA. The concentrations of the monodisperse particles were measured by two CPCs operated in parallel. The same heater described above was mounted upstream of one of the CPCs. The transport efficiency of the heater, given as the particle concentration ratio measured by the two CPCs, was 0.98 for the range of particle diameters between 15 and 100 nm. The size dependence of transport efficiency was not detected in this size range.

Evaporation of volatile aerosol particles in the heating section was characterized by using (NH₄)₂SO₄ particles. Ammonium sulfate particles were generated and size-selected at 30, 50, 100, and 200 nm by the same method used for the calibration of the CCN counter. These particles were introduced to the heater, and the size distributions downstream of the heater were measured by using a DMA and a CPC. Changes in the particle sizes at different temperatures were measured by this system. (NH₄)₂SO₄ particles began to evaporate at 175°C irrespective of their initial diameters. Particles with diameters of 30 and 50 nm (100 and 200 nm) completely evaporated at 200°C (225°C). These evaporation temperatures are similar to those reported previously [Brooks et al., 2002; Paulsen et al., 2006]. This shows the consistency of our VTDMA measurements with previous studies. The size dependence of the evaporation temperature may be due to the kinetics of evaporation. However, this effect was not so significant. Kondo et al. [2006] found that almost all inorganic and organic components, measurable by an Aerodyne aerosol mass spectrometer, evaporated by heating the sample tube at 400°C. They have also observed that mass concentrations of the nonvolatile particles of PM₁₀ have agreed quite well with those of elemental carbon simultaneously measured by a thermal-optical technique, indicating that BC was the main component of nonvolatile cores.

There is a possibility that aerosol components evaporated in the heating section could recondense in the cooling section [Sakurai et al., 2003a; Paulsen et al., 2006]. We have investigated this effect using the measurement system shown in Figure 2b. The heater, DMA, and CPC are the same used for the experiments described above. The thermodenuder (TSI Model 3065) is composed of a heating section and a gas adsorber downstream to remove volatileized compounds. Particles with a diameter of 100 nm were selected by DMA1. If the accumulation of volatileized compounds onto nonvolatile cores is significant, the removal of the recondensed compounds by the thermodenuder will decrease the diameter of the particles measured by the DMA2 and CPC. The temperatures of the thermodenuder were chosen to be room temperature (20°C) and 400°C to detect the possible effect of recondensation onto nonvolatile particles. The change of the mobility diameters caused by the heated thermodenuder was less than 1 nm. The particle concentration in the VTDMA heater (Figure 2a) was much lower (less than 50 particles/cm³ for 100-nm particles) than those of ambient air (~10⁹ particles/cm³ during the experiment) because of the charging efficiency of the charger and the classification by HTDMA. Therefore recondensation is negligible in this study.

The number size distributions of nonvolatile cores at the inlet of DMA3 were derived from the data obtained by DMA3 and CPC2 (Figure 2a) using the STWOM inversion algorithm [Markowski, 1987]. The DMA transfer function developed by Stolzenburg [1988] and the counting efficiency of the CPC were taken into account for this calculation. The validity of the inversion procedure was estimated by TDMA measurement without the heater. The difference of number concentration between the inversion data (TDMA) and the CPC data was less than 1% at all times. The random error of the peak diameter measured by DMA3-CPC2 system was less than 0.2 nm. The systematic difference in diameters was corrected when calculating the change of peak diameter caused by volatilization.

### Field Observations

The observation was made near the urban center of Tokyo during the period 10–17 November 2004. The sampling inlet was located approximately 20 m above ground level, and the instruments were located within a building at the Research Center for Advanced Science and Technology (RCAST) campus of the University of Tokyo (35.66°N, 139.66°E) in Japan. RCAST is located about 10 km west of the Tokyo Bay coastline and is near the southeastern edge of the Kanto Plain. The sampling location and general meteorological conditions are described in detail elsewhere [Kondo et al., 2006]. More detailed descriptions of the operational modes of HTDMA-CCNC/VTDMA system are given by Mochida et al. [2006].

### Definitions of VTDMA Parameters

In this section, some parameters used for the analysis of VTDMA data are defined. Figure 3 shows an example of...
Table 3. The Definitions of Parameters Used for VTDMA Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>Less Volatile (LV)</td>
<td>Particles that have a large (&gt;80 nm) nonvolatile core</td>
</tr>
<tr>
<td>More Volatile (MV)</td>
<td>Particles that have a small (&lt;80 nm) nonvolatile core</td>
</tr>
<tr>
<td>Nonvolatile (NV)</td>
<td>Particles that do not have a nonvolatile core (LV + MV)</td>
</tr>
<tr>
<td>Completely Volatile (CV)</td>
<td>Particles that have a nonvolatile core (LV + MV)</td>
</tr>
<tr>
<td>$F_{LV}$</td>
<td>Number fraction of less volatile particles</td>
</tr>
<tr>
<td>$F_{MV+CV}$</td>
<td>Number fraction of more and completely volatile particles</td>
</tr>
<tr>
<td>$F_{NV}$</td>
<td>Number fraction of nonvolatile particles</td>
</tr>
<tr>
<td>$\Delta d_m$</td>
<td>Change of peak diameter caused by volatilization (in this study, used only for LV)</td>
</tr>
</tbody>
</table>

the VTDMA data in Tokyo. These data were obtained prior to the observation by the HTDMA-CCNC/VTDMA system (see Appendix for more detailed information). The size distribution of the nonvolatile core is bimodal. This bimodal size distribution has been observed at some urban sites, for example, in Leipzig [Philippin et al., 2004] and Aachen [Wehner et al., 2004]. A fraction of 100-nm particles show only a small (less than 20%) shift from their original dry diameter. These particles are mainly composed of nonvolatile composition. This mode is defined as “less volatile” or “LV.” The particles containing relatively small nonvolatile cores are called “more volatile” or “MV.” These definitions have also been used in previous studies [Sakurai et al., 2003a; Wehner et al., 2004].

The normalized size distribution for the less volatile mode is fitted by a Gauss function ($f_{12}$; shaded area in Figure 3). The number fraction of more volatile (MV) and completely volatile (CV) particles ($F_{MV+CV}$) is calculated from the number fraction of less volatile particles ($F_{LV}$).

$$F_{MV+CV} = 1 - F_{LV} \quad (4a)$$

$$F_{LV} = \int f_{12} d\log d_p \quad (4b)$$

The peak diameter of the less volatile mode shows slight changes from its original diameter by volatilization. This decrease in the peak diameter is defined as $\Delta d_m$. Terminology for VTDMA data used in this study is summarized in Table 3.

6. CCN Activity and Volatility of Hygroscopicity-Selected Particle

In this section, results obtained by the HTDMA-CCNC/VTDMA system are discussed. VTDMA and CCN data for hygroscopicity-selected particles are shown in sections 6.1 and 6.2, respectively. Section 6.3 shows the relationship between CCN activity and volatility of hygroscopicity-selected particles.

The hygroscopic growth of 100-nm particles for RH = 83 and 89% averaged over the observation period is plotted in Figure 4. The number size distributions of particles after humidification were bimodal. One was a less hygroscopic (LV) mode, and the other was a more hygroscopic (MH) mode. The volatility and CCN activity of hygroscopicity-selected particles were measured for $g = 1.00$, 1.11, 1.24, and 1.38 particles. For the present study, $g = 1.00$ and 1.11 are defined as less hygroscopic, and $g = 1.24$ and 1.38 are identified as more hygroscopic.

6.1. Volatility of Hygroscopicity-Selected Particles

Average number size distributions of nonvolatile cores measured for different (RH = 83 and 89%) are shown in Figure 5. The dominant part of the less hygroscopic ($g = 1.00$) particles was in the LV mode. It should be noted that less hygroscopic ($g = 1.00$) mode particles contain 10–17% completely volatile particles. Primary particles from lubricant oil emitted from motor vehicles may constitute some portion of these less hygroscopic and completely volatile particles [Sakurai et al., 2003b].

The fraction of MV particles increased with the increase in $g(RH)$. For $g(RH = 83$ and 89%$) = 1.11$, both less volatile and more volatile particles were observed. In particular, for RH = 89%, a distinct peak of the LV mode was observed.

For $g(RH = 83$ and 89%$) = 1.24$ and 1.38, almost all nonvolatile cores were in the MV mode. The size distributions of nonvolatile cores for $g = 1.24$ and 1.38 particles are similar. Therefore it is likely that the hygroscopicity of more hygroscopic particles is mainly controlled by the chemical composition of the volatilized compounds [Mochida et al., 2006]. McMurry et al. [1996] observed by electron microscope that less hygroscopic particles were mainly composed...
Figure 5. Size distribution of non-volatile cores included in hygroscopicity-selected 100-nm particles.
of carbon and that their shapes were irregular, indicating that these particles were predominantly freshly emitted from diesel engines. They also showed that more hygroscopic particles contained sulfur and oxygen. These results are qualitatively consistent with our analysis, which indicates that (1) less hygroscopic particles were mainly composed of BC (LV particles), and (2) BC was not the main component of more hygroscopic particles.

6.2. CCN/CN Ratios of Hygroscopicity-Selected Particles

[28] The CCN/CN values measured as a function of g(RH) are shown in Figure 6. The CCN/CN values generally increased with g(RH). This is qualitatively consistent with the theoretical prediction [e.g., Kreidenweis et al., 2005; Mochida et al., 2006]. For more hygroscopic particles [g(RH = 83 and 89%) = 1.11–1.38], CCN/CN at SS = 0.5% was nearly equal to unity.

[27] At SS = 0.2%, the CCN/CN ratios strongly depended on g. CCN/CN = 0.71 at g(RH = 83%) = 1.24, but it was unity at g(RH = 83%) = 1.38. As discussed in section 2, the critical SS for particle with \( d_{\text{core}} \) < 80 nm (or MV mode) is expected to depend on the chemical composition of coating materials. Considering that g is a good indicator of chemical composition, and the similarity of size distributions of nonvolatile cores (Figure 5), this result shows that CCN/CN (SS = 0.2%) for MV-mode particles is mainly determined by the volatilized aerosol chemical composition. This point is discussed in detail by Mochida et al. [2006].

6.3. CCN Activity of Less Volatile Particles

[28] In this section, dependence of CCN activity of less volatile particles on \( \Delta d_m \) is analyzed. This analysis was performed for g(RH = 83 and 89%) = 1.00 and g(RH = 89%) = 1.11 particles because less volatile peaks were clearly observed in these cases. The temporal variation of CCN/CN, \( F_{MV+CV} \), and \( \Delta d_m \) of less hygroscopic particles \([g(RH = 83%) = 1.00]\) is shown in Figure 7. It can be seen that for \( \Delta d_m < 2–3 \text{ nm} \), CCN/CN (SS = 0.5 and 0.8%) ratios are similar to \( F_{MV+CV} \). This result suggests that the critical SSs of more and completely volatile particles in the less hygroscopic mode were lower than that of less volatile particles. \( \Delta d_m \) increases during the daytime. When \( \Delta d_m > 3 \text{ nm} \), the CCN/CN ratios were often higher than \( F_{MV+CV} \). This feature is more evident for SS = 0.8%. For more quantitative analysis, the number fraction of CCN-active particles of less volatile particles for SS >0.5% was estimated by the following way. We assumed that all of more and completely volatile particles have lower critical SSs than any less volatile particles. Therefore the number fraction of CCN-active less volatile particles in HTDMA-selected particles (including MV and CV particles) is represented as \((\text{CCN/CN}) - F_{MV+CV}\). Then, the ratio of CCN-active LV particles to all LV particles is calculated by dividing \((\text{CCN/CN}) - F_{MV+CV}\) by \( F_{LV} \)

\[
\left(\frac{\text{CCN}}{\text{CN}}\right)_{LV} = \left(\frac{\text{CCN}}{\text{CN}}\right)_{MV+CV} - F_{MV+CV} 

\]

(CCNP/CN)\_LV is positive as long as CCN/CN is larger than \( F_{MV+CV} \).

[29] The (CCNP/CN)\_LV ratios are compared with \( \Delta d_m \) in Figure 8. For SS = 0.5 and 0.8%, (CCNP/CN)\_LV is nearly equal to zero for \( \Delta d_m < 3 \text{ nm} \). It begins to increase at \( \Delta d_m = 4–5 \text{ nm} \) and approaches unity at about 10 nm. The increase of the (CCNP/CN)\_LV is much sharper for SS = 0.8% than for SS = 0.5%. For SS = 1.3%, (CCNP/CN)\_LV was significantly higher than 0 at \( \Delta d_m = 2 \text{ nm} \) and exceeds 0.5 at \( \Delta d_m = 4 \text{ nm} \). The significance of this correlation is well above the precisions of the measurements of the CCN and VTDMA data described in section 3. The main component of nonvolatile core is BC. Therefore this result indicates that the CCN activity of BC particles for SS >0.5% increases with the increase of the coating material. This result is qualitatively consistent with the theoretical prediction (section 2).

[30] In general, BC particles are not spherical in shape [e.g., Park et al., 2004]. In addition, McMurry et al. [1996] showed that the shapes of less hygroscopic particles are chain agglomerates or irregular. Therefore dynamic shape factors before and after the volatilization are required to

![Figure 6. CCN/CN ratios of hygroscopicity-selected 100-nm particles. The upper and lower panels correspond to RH = 89% and RH = 83%, respectively.](image)

![Figure 7. Time series of CCN/CN ratios at SS = 0.5%, 0.8%, and \( F_{MV+CV} \) of 100-nm (g = 1.00 at RH = 83%) particles during November 10-12, 2004. The temporal variation of \( \Delta d_m \) of less-volatile particles is also shown in the figure.](image)
estimate the volume of volatilized materials. However, this kind of knowledge is not currently available. Because of this, it is difficult to interpret the changes of the CCN activity of less volatile particles based on the Köhler theory. [31] Rogak et al. [1993] and Park et al. [2004] have found that the mobility diameter of chain agglomerates is nearly equal to their projected area-equivalent diameter observed by electron microscope. Therefore it may be possible to assume that 10 nm of \(D_{dm}\) is nearly equal to 10 nm changes of the projected area-equivalent diameter.

If aerosol particles are spherical before and after volatilization and if volatile components uniformly coated the nonvolatile core, \(D_{dm} = 10\) nm corresponds to a coating thickness of 5 nm. Spherical particles have the shortest perimeter per unit of projected area among all kinds of shapes. Thus the perimeter of nonspherical particles (for example, chain agglomerates) per unit of projected area is longer than that of spherical particles. Therefore the average coating thickness of nonspherical particles is expected to be thinner than that of spherical particles with the same projected area-equivalent diameter. Thus it is possible to conclude that a slight coating (<5 nm) of volatile compounds on BC significantly increases its CCN activity.

7. Summary and Conclusions

[32] CCN activity and volatility of hygroscopicity-selected 100-nm particles were measured in Tokyo in November 2004 by combining CCNC, VTDMA, and HTDMA. The number size distributions after humidification (RH = 83 and 89%) of these particles were bimodal: less hygroscopic and more hygroscopic modes. These hygroscopicity-selected particles were heated at 400°C to measure the size distributions of their nonvolatile cores. The main component of nonvolatile core at 400°C in Tokyo has been found to be BC. Less hygroscopic mode particles were mostly less volatile. On the other hand, more hygroscopic particles were more and completely volatile.

[33] The less volatile particles in less hygroscopic mode did not act as CCN at SS = 0.5, 0.8, and 1.3% when the

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**Figure 8.** Relationships between (CCN/CN)_{LV} and \(\Delta d_m\) at SS = 0.5%, 0.8%, and 1.3%. Note that lines are guides to the eye.

**Figure A1.** The experimental setup used to measure the VTDMA data shown in Figure 3.

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change of peak diameter caused by volatilization ($\Delta d_m$) was smaller than $\sim$3 nm. By contrast, the CCN/CN ratios of less volatile particles were significantly increased when $\Delta d_m$ was larger than $\sim$3 nm. This result suggests that the CCN activity of BC is highly sensitive to the amount of coating.

Appendix A: VTDMA Measurement Shown in Figure 3

[34] The experimental setup used to measure VTDMA data in Figure 3 is shown in Figure A1. This measurement was performed during 8–9 November 2004 at RCAST (Tokyo). Data were averaged over 2 days.

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