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Title	Dependence of CCN activity of less volatile particles on the amount of coating observed in Tokyo
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Citation	Journal of Geophysical Research, 112, D11207 https://doi.org/10.1029/2006JD007758
Issue Date	2007-06-07
Doc URL	http://hdl.handle.net/2115/26172
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Туре	article (author version)
File Information	JGR112.pdf



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1	<b>Dependence of CCN activity of less-volatile</b>
2	particles on the amount of coating observed in
3	Tokyo
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26	Last modified: January 5, 2007
27	submitted to JGR
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#### 1 Abstract

2 A novel observation system has been developed to measure cloud condensation nuclei (CCN) activity simultaneously with volatility of 3 aerosol particles at 400°C. CCN/CN ratios were measured using a CCN 4 counter and a condensation particle counter, and volatility was measured 5 with a volatility tandem differential mobility analyzer (VTDMA). This 6  $\overline{7}$ system was connected to a hygroscopicity tandem differential mobility 8 analyzer (HTDMA) in tandem to measure these properties of hygroscopicity-selected particles. These instruments were deployed in 9 10 Tokyo in November 2004. In Tokyo, the dominant fraction of non-volatile cores at 400°C has been found to be black carbon (BC). Therefore, the 11number size distribution measured by VTDMA represents the mixing state 1213of black carbon particles. The VTDMA measurement of 14hygroscopicity-selected particles revealed that most of the less-hygroscopic particles were less-volatile, while more-hygroscopic particles were 15more-volatile. CCN/CN ratios of less-volatile particles ((CCN/CN)<sub>LV</sub>) are 16estimated from CCN activity and volatility measurements of 17less-hygroscopic particles.  $(CCN/CN)_{LV}$  at SS  $\geq 0.5\%$  are correlated with 18the decrease of peak diameter due to volatilization  $(\Delta d_m)$ , and  $(CCN/CN)_{LV}$ 19is nearly equal to unity at  $\Delta d_{\rm m} = 10$  nm. This result suggests that the CCN 20activity of BC particles significantly depends on the amount of coating. 2122

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#### 1 **1. Introduction**

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.

Removal of BC is dominated by wet deposition [e.g., Jacobson, 2004]. 9 10 BC particles are hydrophobic and insoluble to water soon after emission because of their graphitic structure. However, it has been shown that BC 11 becomes hydrophilic by surface oxidation [e.g., Zuberi et al., 2005] and 1213hygroscopic by condensation of secondary aerosol components [e.g., 14Saathoff et al., 2003; Sellegri et al., 2003]. Coated BC particles likely act as 15cloud condensation nuclei (CCN), although this point has not been clearly demonstrated by field measurements. 16

Global distributions of BC have been calculated by three-dimensional 17models, which incorporate emissions, transport, and removal of BC [Cooke 18and Wilson, 1996; Chung and Seinfeld, 2005; Park et al., 2005]. One of the 19largest uncertainties in the model calculations is the estimate of the lifetime 20of BC. Almost all BC particles are assumed to be hydrophobic upon emission 21and become hydrophilic by the condensation of secondary aerosol 2223compounds. The timescale of the evolution of BC properties is often given empirically in the form of an e-folding time, although the time scale can vary  $\mathbf{24}$ spatially and temporally [Park et al., 2005]. For more accurate estimates of 25

1 the removal rate of BC, we need to improve our understanding of the coating 2 process of BC and the dependence of its CCN activity on the state of coating. It is advantageous to measure the aging of BC near its source regions 3 considering the anticipated relatively short time-scales for the conversion of 4 BC properties [Saathoff et al., 2003; Park et al., 2005]. In this study,  $\mathbf{5}$ relationships between CCN/CN ratio (CCN activity) and volatility at 400°C 6  $\overline{7}$ were investigated by deploying a CCN counter [Roberts and Nenes, 2005] 8 and a volatility tandem differential mobility analyzer (VTDMA) [Clarke et al., 2004; Philippin et al., 2004] in Tokyo. Kondo et al. [2006] have shown 9 that non-volatile particles at 400°C are nearly equivalent to BC in Tokyo. 10 Therefore we can study the mixing states of BC particles using VTDMA. 11These measurements were performed for particles selected by a 1213hygroscopicity tandem differential mobility analyzer (HTDMA) [Mochida 14et al., 2006].

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#### 16 2. Critical supersaturation of particles containing insoluble cores

For the discussion of the CCN activity of BC, it is useful to calculate the 17CCN activity of a particle composed of an insoluble core and a single 18soluble component coating the core based on the Köhler theory. The 1920equilibrium vapor saturation ratio of water (S) for particles with a dry diameter of  $d_{dry}$  and insoluble core diameter of  $d_{core}$  is expressed as a 21function of the diameter of the droplet  $(D_p)$ , assuming the dry aerosol 22particle, insoluble core, and droplet are spherical in shape [Seinfeld and 23*Pandis*, 1998]  $\mathbf{24}$ 

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1 
$$ln S = \frac{A}{D_p} - \frac{B(d_{dry}^3 - d_{core}^3)}{D_p^3 - d_{dry}^3} \left(A \equiv \frac{4M_w\sigma}{RT\rho_w} B \equiv v \frac{M_w\rho_s}{\rho_w M_s}\right)$$
 (1)

where  $\sigma$  is the surface tension,  $M_w$  and  $M_s$  are the molecular weight of water and solute,  $\rho_w$  and  $\rho_s$  are the density of water and solute, respectively, and v is the van't Hoff factor.

6 The first term on the right-hand side of equation (1) represents the Kelvin 7effect. The Kelvin effect increases the equilibrium vapor pressure of water because of the surface tension of the droplet. The second term on the 8 right-hand side shows Raoult's effect. Raoult's effect decreases the 9 equilibrium vapor pressure due to the mixing of solute. When we consider a 10single particle,  $d_{dry}$  and  $d_{core}$  are constants. In this case, S depends strongly 11 on  $D_p$ , because the variability of A, and B are relatively small. The 12calculated S as a function of  $D_p$ , the so-called Köhler curve, reaches a 13maximum value  $(S_{max})$  at a certain  $D_p$ . The supersaturation (SS) 14corresponding to this value is called the critical supersaturation (critical SS 15 $= (S_{max} - 1))$ . The balance between the Kelvin and Raoult's effects 16determines the critical SS. 17

18Figure 1 shows the critical SS of 100-nm particles as a function of  $d_{core}$ . 19The calculations were made for an insoluble core coated by ammonium 20sulfate and by glutaric acid. The volume fraction of the core  $(V_{core}/V_{total})$  is 21also shown in Figure 1 as a function of  $d_{core}$ . If  $d_{core} < 80$  nm, the volume 22fraction of the coating material is larger than  $V_{\rm core}/V_{\rm total}$ , and the critical SS does not strongly depend on  $d_{core}$ . In this region, the critical SS is mainly 23determined by the chemical composition of the coating material. If  $d_{core} >$ 2480 nm,  $V_{\text{core}}/V_{\text{total}}$  exceeds the volume fraction of the coating material and 25

 $\mathbf{5}$ 

the critical SS increases with the increase of  $d_{core}$ . In this region, SS is sensitive to the amount of coating. Thus  $d_{core} = 80$  nm is a good measure in separating the two regimes for the discussion of the CCN activity of internally mixed aerosol particles with  $d_{dry} = 100$  nm. Table 1 shows the critical SSs of other compounds. Critical SSs are 2.1% at  $d_{core} = 100$  nm for all compounds. In this case, the critical SSs depend only on the Kelvin effect.

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#### 9 **3. Instruments**

10 Figure 2a shows the experimental setup used in this study (HTDMA-CCNC/VTDMA system). In this system, size and mixing state 11(hygroscopicity) of aerosol particles were selected by HTDMA before the 1213measurement of CCN activity and volatility. The HTDMA part of this system 14is 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 15relative humidity (RH) < 4% by a diffusion-dryer. The poly-disperse dry 16particles in the sampled air were charged by a <sup>241</sup>Am bipolar charger, then 17their size was selected by a differential mobility analyzer (DMA1; TSI 18 Model 3081). In this study, the sheath flow to sample flow ratio of all DMAs 19was set at 10:1. Observation results of 100-nm particles were analyzed in 20this study because the number concentration of CCN is highest at 90-140 nm 21during the observation period [Mochida et al., 2006]. Classified particles 22were humidified to grow into larger particles depending on their 23hygroscopicity. The sheath flow of DMA2 was also humidified. The RH in  $\mathbf{24}$ the humidifier and DMA2 were set at 83% or 89% for the present study. The 25

precision of RH was 0.3%. The hygroscopic growth factor, denoted as g
 (RH), is defined as

(2)

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 $\mathbf{5}$ 

6 , where  $d_p(RH)$  is the particles diameter at a given RH.

 $g(RH) = d_p(RH)/d_{drv}$ 

 $\overline{7}$ The voltages applied to DMA2 were fixed to constant values to select 8 particles with the corresponding g (RH) values. This voltage was scanned once per hour to measure the number distribution of g(RH). The humidified 9 10 air was dried again by a Nafion dryer mounted downstream of DMA2. Then, classified dry particles were introduced to CPC1 (TSI model 3022A), a CCN 11 counter (CCNC, Droplet Measurement Technologies) [Roberts and Nenes, 12132005], and a heater. The total number concentration of the mono-disperse 14particle (condensation nuclei; CN) was measured by CPC1, and the CCN number concentrations were measured by the CCNC, respectively. The 15sample flow rate and the sheath flow rate of CCNC were set to 0.05 l/min 16and 0.45 l/min, respectively. The temperature gradient ( $\Delta T$ ) of the thermal 17gradient chamber in the CCNC was periodically cycled at four different 18values (3.6, 7.2, 10.8, and 16.2 K) for the measurements at different SS in 19the chamber. The SS corresponding to these  $\Delta T$  values were calibrated by 20using dried ammonium sulfate  $((NH_4)_2SO_4)$  particles. These particles were 21generated from an aqueous solution of ammonium sulfate by using an 22atomizer (TSI Model 3076). These particles were dried by a diffusion-dryer, 23and size selected by a DMA. Then, they were measured by a CPC and the  $\mathbf{24}$ CCNC to obtain the distributions of CCN/CN ratios. A sigmoid function 25

- 1 (equation (3)) was fitted to the experimental result,
- $\mathbf{2}$

$$3 \qquad \frac{CCN}{CN} = a + \frac{b}{1 + exp(\frac{d_c - d_p}{c})}$$
(3)

where a, b, and c are constants obtained by fitting and  $d_c$  is the center  $\mathbf{5}$ diameter of the sigmoid function.  $d_{\rm c}$  was assumed as the critical dry 6 diameter of ammonium sulfate under the observation conditions. Note that 7the CCN/CN ratio is not necessarily 0.5 at  $d_c$  because of the existence of 8 multiply charged particles and particle loss in the CCNC. In this study, 9 CCN/CN ranged from 0.44 ( $\Delta T = 16.2$  K) to 0.55 ( $\Delta T = 3.6$  K) at  $d_c$ . The 10critical SS corresponding to the observed activation diameter was calculated 11 12by the Köhler theory at a temperature of 308 K. In this calculation, the 13osmotic coefficient of the aqueous solution was calculated by the Pitzer equation [Pitzer and Mayorga, 1973] as described by Mochida et al. [2006]. 14This SS was assumed to be equal to the SS in the CCNC.  $d_c$  and the SS 15corresponding to each  $\Delta T$  are summarized in Table 2. The precisions of the 16CCN and CN number concentrations were estimated to be 2-10% and 1-4% 17from their temporal variation, respectively. Therefore, the precision of 18CCN/CN ratios was calculated to be 2-11%. The CCN/CN ratio for 19ammonium sulfate at 80 nm was 1.01. Therefore, the systematic error in the 20CCN/CN measurement at 100 nm was negligible. 21The VTDMA consisted of a heater, two DMAs (TSI Model 3081), and a 22

23 CPC (TSI Model 3022A). The VTDMA measures size distributions of

24 non-volatile cores of the size-selected particles. The sample air was heated

to 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 non-volatile cores were measured by the DMA3-CPC2 system.

The transport efficiency of particles through the heater is one of the 11 important heater parameters. It was measured using sodium chloride (NaCl) 1213particles because they do not evaporate at 400°C [Brooks et al., 2002; 14Philippin et al., 2004]. Poly-disperse NaCl particles were generated by an 15atomizer, dried by a diffusion-dryer, and size-selected by a DMA. The 16concentrations of the mono-disperse particles were measured by two CPCs 17operated in parallel. The same heater described above was mounted upstream of one of the CPCs. The transport efficiency of the heater, given 18 as the particle concentration ratio measured by the two CPCs, was 0.98 for 1920the range of particle diameters between 15 and 100 nm. The size dependence of transport efficiency was not detected in this size range. 21Evaporation of volatile aerosol particles in the heating section was 22characterized by using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles. Ammonium sulfate particles 23were generated and size-selected at 30, 50, 100, and 200 nm by the same  $\mathbf{24}$ method used for the calibration of the CCN counter. These particles were 25

1 introduced to the heater, and the size distributions downstream of the heater  $\mathbf{2}$ were measured by using a DMA and a CPC. Changes in the particle sizes at different temperatures were measured by this system.  $(NH_4)_2SO_4$  particles 3 began to evaporate at 175 °C irrespective to their initial diameters. Particles 4 with diameters of 30 and 50 nm (100 and 200 nm) completely evaporated at 5 200°C (225°C). These volatilization temperatures are similar to those 6  $\overline{7}$ reported previously [Brooks et al., 2002; Paulsen et al., 2006]. This shows 8 the consistency of our VTDMA measurements with the previous studies. The size dependence of the volatilization temperature may be due to the 9 10 kinetics of volatilization. However, this effect was not so significant. Kondo 11et al. [2006] found that almost all inorganic and organic components measurable by an Aerodyne Aerosol Mass Spectrometer (AMS) evaporated 1213by heating the sample tube at 400 °C. They have also observed that mass 14concentrations of the non-volatile particles of PM<sub>1</sub> have agreed quite well 15with those of elemental carbon simultaneously measured by a thermal-optical technique, indicating that BC was the main component of 1617non-volatile cores.

There is a possibility that aerosol components evaporated in the heating 18 section could re-condense in the cooling section [Sakurai et al., 2003a; 1920Paulsen et al., 2006]. We have investigated this effect using the measurement system shown in Figure 2b. The heater, DMA, and CPC are the 21same used for the experiments described above. The thermodenuder (TSI 2223Model 3065) is composed of a heating section and a gas adsorber downstream to remove volatilized compounds. Particles with a diameter of  $\mathbf{24}$ 100 nm were selected by DMA1. If the accumulation of volatilized 25

1 compounds onto non-volatile cores is significant, removal of the  $\mathbf{2}$ re-condensed compounds by the thermodenuder will decrease the diameter of the particles measured by the DMA2 and CPC. The temperatures of the 3 thermodenuder were chosen to be room temperature  $(20^{\circ}C)$  and  $400^{\circ}C$  to 4 detect the possible effect of re-condensation onto non-volatile particles. 5 The change of the mobility diameters caused by the heated thermodenuder 6  $\overline{7}$ was less than 1 nm. The particle concentration in the VTDMA heater (Figure 2a) was much lower (less than 50 particles/cm<sup>3</sup> for 100-nm 8 particles) than those of ambient air ( $\sim 10^4$  particles/cc during the 9 10 experiment) because of the charging efficiency of the charger and the classification by HTDMA. Therefore, re-condensation is negligible in this 11 12study.

13The number size distributions of non-volatile cores at the inlet of DMA3 14were derived from the data obtained by DMA3 and CPC2 (Figure 2a) using the STWOM inversion algorithm [Markowski, 1987]. The Stolzenburg-type 15DMA transfer function [Stolzenburg, 1988] and the counting efficiency of 1617the CPC were taken into account for this calculation. The validity of the inversion procedure was estimated by TDMA measurement without the 18heater. The difference of number concentration between the inversion data 19(TDMA) and CPC1 data was less than 1% at all times. The random error of 20the peak diameter measured by DMA3-CPC2 system was less than 0.2 nm. 21The systematic difference in diameters was corrected when calculating the 22change of peak diameter caused by volatilization. 23

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#### 25 4. Field observations

1 The observation was made near the urban center of Tokyo during the period November 10-17, 2004. The sampling inlet was located approximately  $\mathbf{2}$ 20 m above ground level, and the instruments were located within a building 3 at the Research Center for Advanced Science and Technology (RCAST) 4 campus of the University of Tokyo (35.66°N, 139.66°E) in Japan. RCAST is 5 located about 10 km west of the Tokyo Bay coastline and is near the 6  $\overline{7}$ southeastern edge of the Kanto Plain. The sampling location and general meteorological conditions are described in detail elsewhere [Kondo et al., 8 2006]. More-detailed descriptions of the operational modes of 9 10 HTDMA-CCNC/VTDMA system are given by Mochida et al. [2006].

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#### 12 **5. Definitions of VTDMA parameters**

13In this section, some parameters used for the analysis of VTDMA data 14are defined. Figure 3 shows an example of the VTDMA data in Tokyo. This data was obtained prior to the observation by the HTDMA-CCNC/VTDMA 15system (See Appendix for more detailed information). The size distribution 16of the non-volatile core is bimodal. This bimodal size distribution has been 17observed at some urban sites, e.g., in Leipzig [Philippin et al., 2004] and 18Aachen [Wehner et al., 2004]. A fraction of 100-nm particles shows only a 1920small (less than 20%) shift from their original dry diameter. These particles are mainly composed by non-volatile composition. This mode is defined as 21'less-volatile' or 'LV'. The particles containing relatively small 22non-volatile cores are called 'more-volatile' or 'MV'. These definitions 23have also been used in previous studies [Sakurai et al., 2003a; Wehner et al.,  $\mathbf{24}$ 2004]. 25

1 The number fraction of particles containing a non-volatile core  $(F_{NV})$  was 2 defined as the ratio of the number concentrations measured by VTDMA to those by CPC1. Some particles do not have the non-volatile cores measurable 3 by the VTDMA (<15 nm). This fraction was defined as 'completely volatile' 4 or 'CV.' 5

The normalized size distribution for the less-volatile mode is fitted by a 6  $\overline{7}$ Gauss function (f<sub>fit</sub>; shaded area in Figure 3). The number fraction of more-volatile (MV) and completely volatile (CV) particles ( $F_{MV + CV}$ ) is 8 calculated from the number fraction of less-volatile particles ( $F_{LV}$ ). 9

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11

11 
$$F_{\rm MV + CV} = 1 - F_{\rm LV}$$
 (4a)

12

13 
$$F_{\rm LV} = \int f_{fit} d \log d_p \tag{4b}$$

14

The peak diameter of the less-volatile mode shows slight changes from its 1516original diameter by volatilization. This decrease in the peak diameter is 17defined as  $\Delta d_{\rm m}$ . Terminology for VTDMA data used in this study is 18summarized in table 3.

19

#### 6. CCN activity and volatility of hygroscopicity-selected particle 20

In this section, results obtained by the HTDMA-CCNC/VTDMA system 21are discussed. VTDMA and CCN data for hygroscopicity-selected particles 22are shown in section 6.1 and section 6.2, respectively. Section 6.3 shows the 23relationship between CCN activity and volatility of hygroscopicity-selected 24particles. 25

1 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  $\mathbf{2}$ distributions of particles after humidification were bi-modal. One was a 3 less-hygroscopic (LH) mode and the other was a more-hygroscopic (MH) 4 mode. The volatility and CCN activity of hygroscopicity-selected particles  $\mathbf{5}$ were measured for g = 1.00, 1.11, 1.24, and 1.38 particles. For the present 6  $\overline{7}$ study, g = 1.00 and 1.11 are defined as less-hygroscopic, and g = 1.24 and 8 1.38 as more-hygroscopic.

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- 10

#### 11 6.1 Volatility of hygroscopicity-selected particles

Average number size distributions of non-volatile cores measured for different g (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 non-volatile cores were in the MV mode. The size distributions of non-volatile cores for g = 1.24 and 1.38 particle are similar. Therefore it is likely that the

1 hygroscopicity of more-hygroscopic particles is mainly controlled by the  $\mathbf{2}$ chemical composition of the volatilized compounds [Mochida et al., 2006]. McMurry et al. [1996] observed by electron microscope that 3 less-hygroscopic particles were mainly composed of carbon and that their 4 shapes were irregular, indicating that these particles were predominantly 5 freshly emitted from diesel engines. They also showed that 6  $\overline{7}$ more-hygroscopic particles contained sulfur and oxygen. These results are qualitatively consistent with our analysis, which indicates that 1) 8 less-hygroscopic particles were mainly composed of BC (LV particles), and 9 10 2) BC was not the main component of more-hygroscopic particles. 11126.2 CCN/CN ratios of hygroscopicity-selected particles 13The CCN/CN values measured as a function of g (RH) are shown in 14Figure 6. The CCN/CN values generally increased with g (RH). This is qualitatively consistent with the theoretical prediction [e.g., Kreidenweis et 15al., 2005; Mochida et al., 2006]. For more-hygroscopic particles (g (RH = 1683% and 89%) = 1.11-1.38), CCN/CN at SS = 0.5% was nearly equal to 17unity. 18At SS = 0.2%, the CCN/CN ratios strongly depended on g. CCN/CN =190.71 at g (RH = 83%) = 1.24, but it was unity at g (RH = 83%) = 1.38. As 20discussed in section 2, the critical SS for particle with  $d_{core} < 80$  nm (or MV 21mode) is expected to depend on the chemical composition of coating 2223materials. Considering that g is a good indicator of chemical composition,

and the similarity of size distributions of non-volatile 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).

3

### 4 6.3 CCN activity of less-volatile particles

In this section, dependence of CCN activity of less-volatile particles on  $\mathbf{5}$  $\Delta d_{\rm m}$  is analyzed. This analysis was performed for g (RH = 83% and 89%) = 6  $\overline{7}$ 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,  $F_{MV+}$ 8 <sub>CV</sub>, and  $\Delta d_{\rm m}$  of less-hygroscopic particles (g (RH = 83%) = 1.00) is shown in 9 Figure 7. It can be seen that for  $\Delta d_{\rm m} < 2$ -3nm, CCN/CN (SS = 0.5% and 100.8%) ratios are similar to  $F_{MV + CV}$ . This result suggests that the critical SSs 11of more- and completely volatile particles in the less-hygroscopic mode 1213were lower than that of less-volatile particles.  $\Delta d_{\rm m}$  increases during the 14daytime. When  $\Delta d_{\rm m} > 3$  nm, the CCN/CN ratios were often higher than  $F_{\rm MV}$  $_{+ CV}$ . This feature is more evident for SS = 0.8%. For more-quantitative 15analysis, the number fraction of CCN active particles of less-volatile 16particles for SS >0.5% was estimated by the following way. We assumed 17that all of more- and completely volatile particles have lower critical SSs 18than any less-volatile particles. Therefore, the number fraction of CCN 19active less-volatile particles in HTDMA selected particles (including MV 20and CV particles) is represented as (CCN/CN) -  $F_{MV+CV}$ . Then, the ratio of 21CCN active LV particles to all LV particles is calculated by dividing 22(CCN/CN) -  $F_{MV+CV}$  by  $F_{LV}$ 23

24

$$1 \qquad \left(\frac{CCN}{CN}\right)_{LV} = \frac{\left(\frac{CCN}{CN}\right) - F_{MV+CV}}{F_{LV}} \tag{5}.$$

 $\mathbf{2}$ 

3  $(CCN/CN)_{LV}$  is positive as long as CCN/CN is larger than  $F_{MV+CV}$ . The  $(CCN/CN)_{LV}$  ratios are compared with  $\Delta d_m$  in Figure 8. For SS = 4 0.5% and 0.8%, (CCN/CN)<sub>LV</sub> is nearly equal to zero for  $\Delta d_{\rm m} < 3$  nm. It  $\mathbf{5}$ begins to increase at  $\Delta d_{\rm m} = 4-5$  nm and approaches unity at about 10 nm. 6 The increase of the  $(CCN/CN)_{LV}$  is much sharper for SS = 0.8 % than for SS 7= 0.5%. For SS = 1.3%,  $(CCN/CN)_{LV}$  was significantly higher than zero at 8  $\Delta d_m = 2$  nm and exceeds 0.5 at  $\Delta d_m = 4$  nm. The significance of this 9 correlation is well above the precisions of the measurements of the CCN 10and VTDMA data described in section 3. The main component of 11 12non-volatile core is BC. Therefore, this result indicates that the CCN 13activity of BC particles for SS > 0.5% increases with the increase of the coating material. This result is qualitatively consistent with the theoretical 14prediction (section 2). 15In general, BC particles are not spherical in shape [e.g., Park et al., 2004]. 16In addition, McMurry et al. [1996] showed that the shapes of 17less-hygroscopic particles are chain agglomerates or irregular. Therefore, 18dynamic shape factors before and after the volatilization are required to 19estimate the volume of volatilized materials. However, this kind of 20knowledge is not currently available. Because of this, it is difficult to 21

22interpret the changes of the CCN activity of less-volatile particles based on the Köhler theory. 23



Rogak et al. [1993] and Park et al. [2004] have found that the mobility

1 diameter of chain agglomerates is nearly equal to its projected area  $\mathbf{2}$ equivalent diameter observed by electron microscope. Therefore it may be possible to assume that 10 nm of  $\Delta d_{\rm m}$  is nearly equal to 10 nm changes of 3 the projected area equivalent diameter. If aerosol particles are spherical 4before and after volatilization and volatile components uniformly coated the  $\mathbf{5}$ non-volatile core,  $\Delta d_{\rm m} = 10$  nm corresponds to a coating thickness of 5 nm. 6  $\overline{7}$ Spherical particles have the shortest perimeter per unit of projected area 8 among all kinds of shapes. Thus, the perimeter of non-spherical particles (e.g., chain agglomerates) per unit of projected area is longer than that of 9 10 spherical particles. Therefore, the average coating thickness of non-spherical particles is expected to be thinner than that of spherical 11particles with the same projected area equivalent diameter. Thus, it is 1213possible to conclude that a slight coating (< 5 nm) of volatile compounds on BC significantly increases its CCN activity. 14

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#### 1 7. Summary and conclusions

2 CCN activity and volatility of hygroscopicity-selected 100-nm particles were measured in Tokyo in November 2004 by combining a CCNC, VTDMA, 3 and HTDMA. The number size distributions after humidification (RH = 83) 4 and 89%) of these particles were bimodal: less-hygroscopic and  $\mathbf{5}$ more-hygroscopic modes. These hygroscopicity-selected particles were 6  $\overline{7}$ heated to 400°C to measure the size distributions of their non-volatile cores. The main component of non-volatile core at 400°C in Tokyo has been found 8 to be BC. Less-hygroscopic mode particles were mostly less-volatile. On 9 10 the other hand, more-hygroscopic particles were more- and 11completely-volatile. 12The less-volatile particles in less-hygroscopic mode did not act as CCN at 13SS = 0.5, 0.8, and 1.3% when the change of peak diameter caused by volatilization ( $\Delta d_m$ ) was smaller than ~3 nm. By contrast, the CCN/CN 1415ratios of less volatile particles were significantly increased when  $\Delta d_m$  was larger than ~3 nm. This result suggests that the CCN activity of BC is 1617highly sensitive to the amount of coating. 18

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2	Acknowledgments. This work was supported by the Ministry of Education,
3	Culture, Sports, Science, and Technology (MEXT), the Japanese Science
4	and Technology Agency (JST), and the global environment research fund of
<b>5</b>	the Japanese Ministry of the Environment. The measurements at RCAST in
6	Tokyo were made as a part of Integrated Measurement Program for Aerosol
7	and Oxidant Chemistry in Tokyo (IMPACT) campaigns. The IMPACT
8	campaigns were conducted within the framework of the International Global
9	Atmospheric Chemistry Project (IGAC), Mega-Cities: Asia. M. Kuwata
10	thanks the Japan Society for the Promotion of Science (JSPS) for JSPS
11	Research Fellowships for Young Scientists.
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10	Appendix
11	VTDMA measurement shown in Figure 3
12	The experimental setup used to measure VTDMA data in Figure 3 is shown
13	in Figure A1. This measurement was performed during November 8-9, 2004
14	at RCAST (Tokyo). Data was averaged over two days.
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#### **1** Figure Captions

Figure 1. Relationships between the size of insoluble cores and critical  $\mathbf{2}$ supersaturations (critical SSs). The calculation was performed for particles 3 with a dry diameter of 100 nm. The solid line shows the critical SSs of 4 particles composed of ammonium sulfate (coating material) and an  $\mathbf{5}$ insoluble core. The critical SSs of particles coated by glutaric acid are 6  $\overline{7}$ shown as the dashed line. The volume fraction of insoluble cores  $(V_{core})$  is 8 also shown in this figure. In the region where the core diameter is larger than 80nm, critical supersaturation strongly depends on core size. In the 9 10 other region (core diameter < 80 nm) critical supersaturation is controlled by the solute composition. 11 1213Figure 2. a) HTDMA-CCNC/VTDMA system used in this study. b) The 14experimental setup used for the inspection of re-condensation of the heater. 15Figure 3. An example of VTDMA data in Tokyo and the definitions of 16less-volatile and more-volatile particles 1718Figure 4. Average distribution of hygroscopic growth of 100-nm particles at 19RH = 83% (November 10-15, 2004) and at RH = 89% (November 17). The 20hygroscopic growth factor (g) is shown in upper part of the figure. 2122Figure 5. Size distribution of non-volatile cores included in 23hygroscopicity-selected 100-nm particles. 2425

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Figure 6. CCN/CN ratios of hygroscopicity-selected 100-nm particles. The
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     upper and lower panels correspond to RH = 89\% and RH = 83\%,
 \mathbf{2}
     respectively.
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     Figure 7. Time series of CCN/CN ratios at SS = 0.5%, 0.8%, and F_{MV+CV} of
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     100-nm (g = 1.00 at RH = 83%) particles during November 10-12, 2004.
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     The temporal variation of \Delta d_{\rm m} of less-volatile particles is also shown in the
 \overline{7}
     figure.
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     Figure 8. Relationships between (CCN/CN)_{LV} and \Delta d_m at SS = 0.5%, 0.8%,
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11
     and 1.3%. Note that lines are guides to the eye.
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     Figure A1. The experimental setup used to measure the VTDMA data shown
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     in Figure 3.
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- Table 1. Critical supersaturations (critical SSs) of 100-nm particles
   composed of an insoluble core and a single soluble coating compound.
   d<sub>core</sub> is the diameter of the insoluble core. SS reported in %.

7	Compound	$d_{\rm core} = 0 {\rm nm}$	20 nm	40 nm	60 nm	80 nm	100 nm
8	Ammonium sulfate	0.14	0.14	0.14	0.15	0.19	2.1
9	Ammonium nitrate	0.13	0.13	0.14	0.15	0.19	2.1
10	Malonic acid	0.22	0.22	0.23	0.25	0.31	2.1
11	Glutaric acid	0.26	0.26	0.27	0.30	0.37	2.1
12	Levoglucosan	0.27	0.27	0.28	0.31	0.39	2.1
13							
14							
15							

ΔT (K)	$d_{\rm c} ({\rm nm})$	Critical SS (%)
3.6	74	0.2
7.2	41	0.5
0.8	31	0.8
6.2	23	1.3

Table 2. Activation diameters of ammonium sulfate particles and
 corresponding SSs at each temperature gradient.

Less-volatile (LV)	Particles that have a large (> 80 nm) non-volatile core
More-volatile (MV)	Particles that have a small (< 80 nm) non-volatile core
Non-volatile (NV)	Particles that have a non-volatile core (LV + MV)
Completely volatile (CV)	Particles that do not have a non-volatile core
$F_{ m LV}$	Number fraction of less-volatile particles
$F_{\rm MV+CV}$	Number fraction of more- and completely volatile particles
$F_{ m NV}$	Number fraction of non-volatile particles
$\Delta d_{ m m}$	Change of peak diameter caused by volatilization (in this study, used only for LV)



Figure 1



# **b)** Thermodenuder TDMA system

Ambient air Heater 241Am DMA1 Thermodenuder DMA2 CPC

Figure 2



Figure 3



Figure 4



Figure 5



Figure 5 (continued)



Figure 6



Figure 7



Figure 8



Figure A1