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1 **Dependence of CCN activity of less-volatile**
2 **particles on the amount of coating observed in**
3 **Tokyo**

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5 M. Kuwata*¹, Y. Kondo¹, M. Mochida^{2†}, N. Takegawa¹, and K.Kawamura²

6
7 1. Research Center for Advanced Science and Technology, the University of
8 Tokyo, Tokyo, Japan

9 2. Institute of Low Temperature Science, Hokkaido University, Sapporo,
10 Japan

11
12 † Now at Institute for Advanced Research, Nagoya University, Nagoya,
13 Japan

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19
20 * Corresponding author

21 e-mail: kuwata@atmos.rcast.u-tokyo.ac.jp

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1 **Abstract**

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

22

1 **1. Introduction**

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

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

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

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.

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

15

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

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

25

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

2

3 where σ is the surface tension, M_w and M_s are the molecular weight of water
 4 and solute, ρ_w and ρ_s are the density of water and solute, respectively, and v
 5 is the van't Hoff factor.

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

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

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

8

9 **3. Instruments**

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

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

$$3 \quad g(\text{RH}) = d_p(\text{RH})/d_{\text{dry}} \quad (2)$$

4
5
6 , where $d_p(\text{RH})$ is the particles diameter at a given RH.

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
9 once per hour to measure the number distribution of $g(\text{RH})$. The humidified
10 air was dried again by a Nafion dryer mounted downstream of DMA2. Then,
11 classified dry particles were introduced to CPC1 (TSI model 3022A), a CCN
12 counter (CCNC, Droplet Measurement Technologies) [Roberts and Nenes,
13 2005], and a heater. The total number concentration of the mono-disperse
14 particle (condensation nuclei; CN) was measured by CPC1, and the CCN
15 number concentrations were measured by the CCNC, respectively. The
16 sample flow rate and the sheath flow rate of CCNC were set to 0.05 l/min
17 and 0.45 l/min, respectively. The temperature gradient (ΔT) of the thermal
18 gradient chamber in the CCNC was periodically cycled at four different
19 values (3.6, 7.2, 10.8, and 16.2 K) for the measurements at different SS in
20 the chamber. The SS corresponding to these ΔT values were calibrated by
21 using dried ammonium sulfate ((NH₄)₂SO₄) particles. These particles were
22 generated from an aqueous solution of ammonium sulfate by using an
23 atomizer (TSI Model 3076). These particles were dried by a diffusion-dryer,
24 and size selected by a DMA. Then, they were measured by a CPC and the
25 CCNC to obtain the distributions of CCN/CN ratios. A sigmoid function

1 (equation (3)) was fitted to the experimental result,

2

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

4

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

22 The VTDMA consisted of a heater, two DMAs (TSI Model 3081), and a
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

1 to 400°C by a mantle heater wrapped around a stainless steel tube (3/8-inch
2 outer diameter, 7-mm inner diameter, and 21 cm long). A thermocouple was
3 attached to the outer wall at the center of the heated section. A
4 proportional-integral-derivative (PID) controller (CAL3200, CAL controls)
5 was used to maintain the temperature of the heater at 400±1°C. The average
6 residence time of the sample air through the heated section was estimated to
7 be 1.6 s at room temperature at the sample flow rate of 0.3 l/min. Particles
8 with diameters prescribed by DMA1 lost their volatile components in the
9 heated section. The size distributions of residual non-volatile cores were
10 measured by the DMA3-CPC2 system.

11 The transport efficiency of particles through the heater is one of the
12 important heater parameters. It was measured using sodium chloride (NaCl)
13 particles because they do not evaporate at 400°C [*Brooks et al.*, 2002;
14 *Philippin et al.*, 2004]. Poly-disperse NaCl particles were generated by an
15 atomizer, dried by a diffusion-dryer, and size-selected by a DMA. The
16 concentrations of the mono-disperse particles were measured by two CPCs
17 operated in parallel. The same heater described above was mounted
18 upstream of one of the CPCs. The transport efficiency of the heater, given
19 as the particle concentration ratio measured by the two CPCs, was 0.98 for
20 the range of particle diameters between 15 and 100 nm. The size
21 dependence of transport efficiency was not detected in this size range.

22 Evaporation of volatile aerosol particles in the heating section was
23 characterized by using (NH₄)₂SO₄ particles. Ammonium sulfate particles
24 were generated and size-selected at 30, 50, 100, and 200 nm by the same
25 method used for the calibration of the CCN counter. These particles were

1 introduced to the heater, and the size distributions downstream of the heater
2 were measured by using a DMA and a CPC. Changes in the particle sizes at
3 different temperatures were measured by this system. $(\text{NH}_4)_2\text{SO}_4$ particles
4 began to evaporate at 175 °C irrespective to their initial diameters. Particles
5 with diameters of 30 and 50 nm (100 and 200 nm) completely evaporated at
6 200°C (225°C). These volatilization temperatures are similar to those
7 reported previously [*Brooks et al.*, 2002; *Paulsen et al.*, 2006]. This shows
8 the consistency of our VTDMA measurements with the previous studies.
9 The size dependence of the volatilization temperature may be due to the
10 kinetics of volatilization. However, this effect was not so significant. *Kondo*
11 *et al.* [2006] found that almost all inorganic and organic components
12 measurable by an Aerodyne Aerosol Mass Spectrometer (AMS) evaporated
13 by heating the sample tube at 400 °C. They have also observed that mass
14 concentrations of the non-volatile particles of PM_{10} have agreed quite well
15 with those of elemental carbon simultaneously measured by a
16 thermal-optical technique, indicating that BC was the main component of
17 non-volatile cores.

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

1 compounds onto non-volatile cores is significant, removal of the
2 re-condensed compounds by the thermodenuder will decrease the diameter
3 of the particles measured by the DMA2 and CPC. The temperatures of the
4 thermodenuder were chosen to be room temperature (20°C) and 400°C to
5 detect the possible effect of re-condensation onto non-volatile particles.
6 The change of the mobility diameters caused by the heated thermodenuder
7 was less than 1 nm. The particle concentration in the VTDMA heater
8 (Figure 2a) was much lower (less than 50 particles/cm³ for 100-nm
9 particles) than those of ambient air (~10⁴ particles/cc during the
10 experiment) because of the charging efficiency of the charger and the
11 classification by HTDMA. Therefore, re-condensation is negligible in this
12 study.

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

24

25 **4. Field observations**

1 The observation was made near the urban center of Tokyo during the
2 period November 10-17, 2004. The sampling inlet was located approximately
3 20 m above ground level, and the instruments were located within a building
4 at the Research Center for Advanced Science and Technology (RCAST)
5 campus of the University of Tokyo (35.66°N, 139.66°E) in Japan. RCAST is
6 located about 10 km west of the Tokyo Bay coastline and is near the
7 southeastern edge of the Kanto Plain. The sampling location and general
8 meteorological conditions are described in detail elsewhere [*Kondo et al.*,
9 2006]. More-detailed descriptions of the operational modes of
10 HTDMA-CCNC/VTDMA system are given by *Mochida et al.* [2006].
11

12 **5. Definitions of VTDMA parameters**

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

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
3 those by CPC1. Some particles do not have the non-volatile cores measurable
4 by the VTDMA (<15 nm). This fraction was defined as ‘completely volatile’
5 or ‘CV.’

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

10

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

12

$$13 \quad F_{LV} = \int f_{fit} d \log d_p \quad (4b)$$

14

15 The peak diameter of the less-volatile mode shows slight changes from its
16 original diameter by volatilization. This decrease in the peak diameter is
17 defined as Δd_m . Terminology for VTDMA data used in this study is
18 summarized in table 3.

19

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

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

1 The hygroscopic growth of 100-nm particles for RH = 83% and 89%
2 averaged over the observation period is plotted in Figure 4. The number size
3 distributions of particles after humidification were bi-modal. One was a
4 less-hygroscopic (LH) mode and the other was a more-hygroscopic (MH)
5 mode. The volatility and CCN activity of hygroscopicity-selected particles
6 were measured for $g = 1.00, 1.11, 1.24,$ and 1.38 particles. For the present
7 study, $g = 1.00$ and 1.11 are defined as less-hygroscopic, and $g = 1.24$ and
8 1.38 as more-hygroscopic.

9
10

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

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

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

23 For g (RH = 83% and 89%) = 1.24 and 1.38 , almost all non-volatile cores
24 were in the MV mode. The size distributions of non-volatile cores for $g =$
25 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
2 chemical composition of the volatilized compounds [Mochida *et al.*, 2006].
3 McMurry *et al.* [1996] observed by electron microscope that
4 less-hygroscopic particles were mainly composed of carbon and that their
5 shapes were irregular, indicating that these particles were predominantly
6 freshly emitted from diesel engines. They also showed that
7 more-hygroscopic particles contained sulfur and oxygen. These results are
8 qualitatively consistent with our analysis, which indicates that 1)
9 less-hygroscopic particles were mainly composed of BC (LV particles), and
10 2) BC was not the main component of more-hygroscopic particles.

11

12 **6.2 CCN/CN ratios of hygroscopicity-selected particles**

13 The CCN/CN values measured as a function of g (RH) are shown in
14 Figure 6. The CCN/CN values generally increased with g (RH). This is
15 qualitatively consistent with the theoretical prediction [e.g., Kreidenweis *et*
16 *al.*, 2005; Mochida *et al.*, 2006]. For more-hygroscopic particles (g (RH =
17 83% and 89%) = 1.11-1.38), CCN/CN at SS = 0.5% was nearly equal to
18 unity.

19 At SS = 0.2%, the CCN/CN ratios strongly depended on g . CCN/CN =
20 0.71 at g (RH =83%) = 1.24, but it was unity at g (RH =83%) = 1.38. As
21 discussed in section 2, the critical SS for particle with $d_{\text{core}} < 80$ nm (or MV
22 mode) is expected to depend on the chemical composition of coating
23 materials. Considering that g is a good indicator of chemical composition,
24 and the similarity of size distributions of non-volatile cores (Figure 5), this
25 result shows that CCN/CN (SS = 0.2%) for MV-mode particles is mainly

1 determined by the volatilized aerosol chemical composition. This point is
2 discussed in detail by *Mochida et al.*(2006).

3

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

5 In this section, dependence of CCN activity of less-volatile particles on
6 Δd_m is analyzed. This analysis was performed for g (RH = 83% and 89%) =
7 1.00 and g (RH = 89%) = 1.11 particles, because less-volatile peaks were
8 clearly observed in these cases. The temporal variation of CCN/CN, $F_{MV +$
9 $CV}$, and Δd_m of less-hygroscopic particles (g (RH = 83%) = 1.00) is shown in
10 Figure 7. It can be seen that for $\Delta d_m < 2-3\text{nm}$, CCN/CN (SS = 0.5% and
11 0.8%) ratios are similar to $F_{MV + CV}$. This result suggests that the critical SSs
12 of more- and completely volatile particles in the less-hygroscopic mode
13 were lower than that of less-volatile particles. Δd_m increases during the
14 daytime. When $\Delta d_m > 3 \text{ nm}$, the CCN/CN ratios were often higher than F_{MV}
15 $+ CV$. This feature is more evident for SS = 0.8%. For more-quantitative
16 analysis, the number fraction of CCN active particles of less-volatile
17 particles for SS >0.5% was estimated by the following way. We assumed
18 that all of more- and completely volatile particles have lower critical SSs
19 than any less-volatile particles. Therefore, the number fraction of CCN
20 active less-volatile particles in HTDMA selected particles (including MV
21 and CV particles) is represented as $(\text{CCN/CN}) - F_{MV+CV}$. Then, the ratio of
22 CCN active LV particles to all LV particles is calculated by dividing
23 $(\text{CCN/CN}) - F_{MV+CV}$ by F_{LV}

24

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

(CCN/CN)_{LV} is positive as long as CCN/CN is larger than F_{MV+CV} .

The (CCN/CN)_{LV} ratios are compared with Δd_m in Figure 8. For SS = 0.5% and 0.8%, (CCN/CN)_{LV} is nearly equal to zero for $\Delta d_m < 3$ nm. It begins to increase at $\Delta d_m = 4$ -5 nm and approaches unity at about 10 nm. The increase of the (CCN/CN)_{LV} is much sharper for SS = 0.8 % than for SS = 0.5%. For SS = 1.3%, (CCN/CN)_{LV} was significantly higher than zero at $\Delta d_m = 2$ nm and exceeds 0.5 at $\Delta d_m = 4$ 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 non-volatile 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).

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 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.

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
2 equivalent diameter observed by electron microscope. Therefore it may be
3 possible to assume that 10 nm of Δd_m is nearly equal to 10 nm changes of
4 the projected area equivalent diameter. If aerosol particles are spherical
5 before and after volatilization and volatile components uniformly coated the
6 non-volatile core, $\Delta d_m = 10$ nm corresponds to a coating thickness of 5 nm.
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
9 (e.g., chain agglomerates) per unit of projected area is longer than that of
10 spherical particles. Therefore, the average coating thickness of
11 non-spherical particles is expected to be thinner than that of spherical
12 particles with the same projected area equivalent diameter. Thus, it is
13 possible to conclude that a slight coating (< 5 nm) of volatile compounds on
14 BC significantly increases its CCN activity.

15

16

7. Summary and conclusions

CCN activity and volatility of hygroscopicity-selected 100-nm particles were measured in Tokyo in November 2004 by combining a 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 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 to be BC. Less-hygroscopic mode particles were mostly less-volatile. On the other hand, more-hygroscopic particles were more- and completely-volatile.

The less-volatile particles in less-hygroscopic mode did not act as CCN at SS = 0.5, 0.8, and 1.3% when the change of peak diameter caused by volatilization (Δd_m) was smaller than ~3 nm. By contrast, the CCN/CN ratios of less volatile particles were significantly increased when Δd_m was larger than ~3 nm. This result suggests that the CCN activity of BC is highly sensitive to the amount of coating.

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Author Addresses:

M. Kuwata, Y. Kondo, and N. Takegawa, Research Center for Advanced Science and Technology, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan. (kuwata@atmos.rcast.u-tokyo.ac.jp, kondo@atmos.rcast.u-tokyo.ac.jp, takegawa@atmos.rcast.u-tokyo.ac.jp)
M. Mochida, Institute for Advanced Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan (e-mail: mochida@iar.nagoya-u.ac.jp)
K. Kawamura, Institute of Low Temperature Science, Hokkaido University, N19 W8, Kita-ku, Sapporo 060-0819, Japan (kawamura@pop.lowtem.hokudai.ac.jp)

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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**

2 **Figure 1.** Relationships between the size of insoluble cores and critical
3 supersaturations (critical SSs). The calculation was performed for particles
4 with a dry diameter of 100 nm. The solid line shows the critical SSs of
5 particles composed of ammonium sulfate (coating material) and an
6 insoluble core. The critical SSs of particles coated by glutaric acid are
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
9 than 80nm, critical supersaturation strongly depends on core size. In the
10 other region (core diameter < 80 nm) critical supersaturation is controlled
11 by the solute composition.

12

13 **Figure 2.** a) HTDMA-CCNC/VTDMA system used in this study. b) The
14 experimental setup used for the inspection of re-condensation of the heater.

15

16 **Figure 3.** An example of VTDMA data in Tokyo and the definitions of
17 less-volatile and more-volatile particles

18

19 **Figure 4.** Average distribution of hygroscopic growth of 100-nm particles at
20 RH = 83% (November 10-15, 2004) and at RH = 89% (November 17). The
21 hygroscopic growth factor (g) is shown in upper part of the figure.

22

23 **Figure 5.** Size distribution of non-volatile cores included in
24 hygroscopicity-selected 100-nm particles.

25

1 **Figure 6.** CCN/CN ratios of hygroscopicity-selected 100-nm particles. The
2 upper and lower panels correspond to RH = 89% and RH = 83%,
3 respectively.

4
5 **Figure 7.** Time series of CCN/CN ratios at SS = 0.5%, 0.8%, and $F_{MV + CV}$ of
6 100-nm ($g = 1.00$ at RH = 83%) particles during November 10-12, 2004.
7 The temporal variation of Δd_m of less-volatile particles is also shown in the
8 figure.

9
10 **Figure 8.** Relationships between $(CCN/CN)_{LV}$ and Δd_m at SS = 0.5%, 0.8%,
11 and 1.3%. Note that lines are guides to the eye.

12
13 **Figure A1.** The experimental setup used to measure the VTDMA data shown
14 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_{core} is the diameter of the insoluble core. SS reported in %.

Compound	$d_{\text{core}} = 0$ nm	20 nm	40 nm	60 nm	80 nm	100 nm
Ammonium sulfate	0.14	0.14	0.14	0.15	0.19	2.1
Ammonium nitrate	0.13	0.13	0.14	0.15	0.19	2.1
Malonic acid	0.22	0.22	0.23	0.25	0.31	2.1
Glutaric acid	0.26	0.26	0.27	0.30	0.37	2.1
Levogluconan	0.27	0.27	0.28	0.31	0.39	2.1

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

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ΔT (K)	d_c (nm)	Critical SS (%)
3.6	74	0.2
7.2	41	0.5
10.8	31	0.8
16.2	23	1.3

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Table 3: The definitions of parameters used for VTDMA data

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_{LV}	Number fraction of less-volatile particles
F_{MV+CV}	Number fraction of more- and completely volatile particles
F_{NV}	Number fraction of non-volatile particles
Δd_m	Change of peak diameter caused by volatilization (in this study, used only for LV)

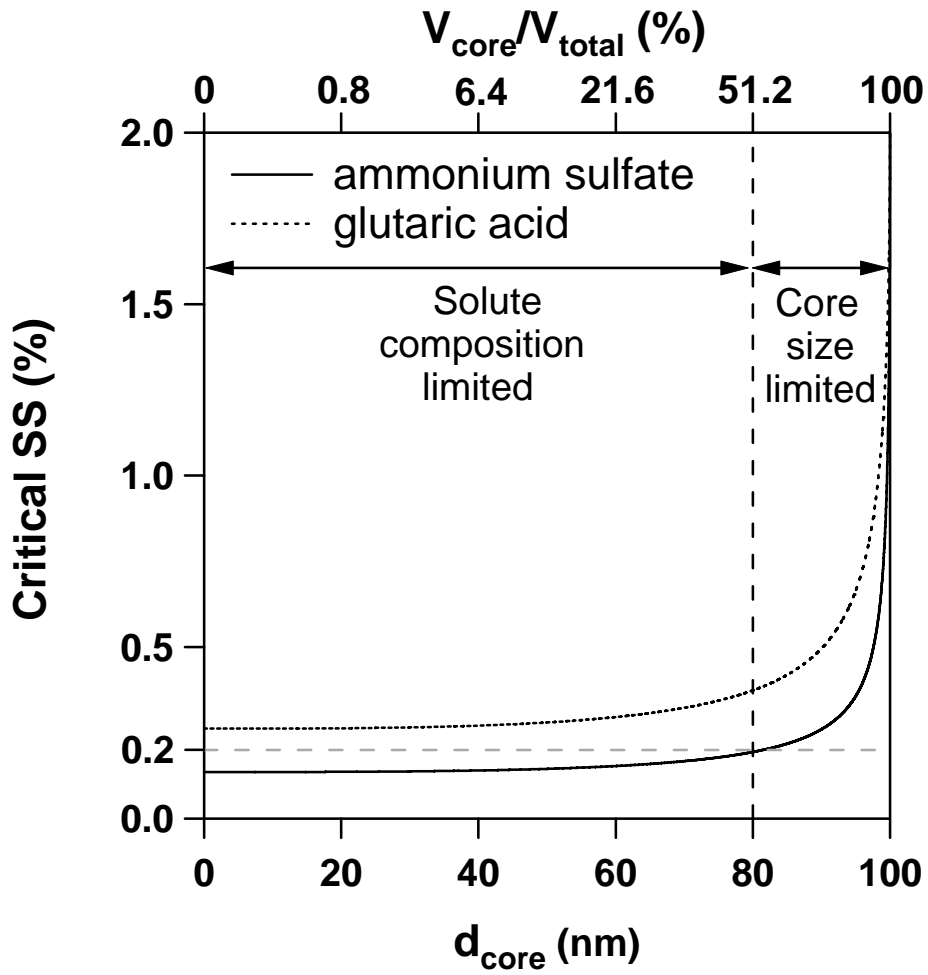
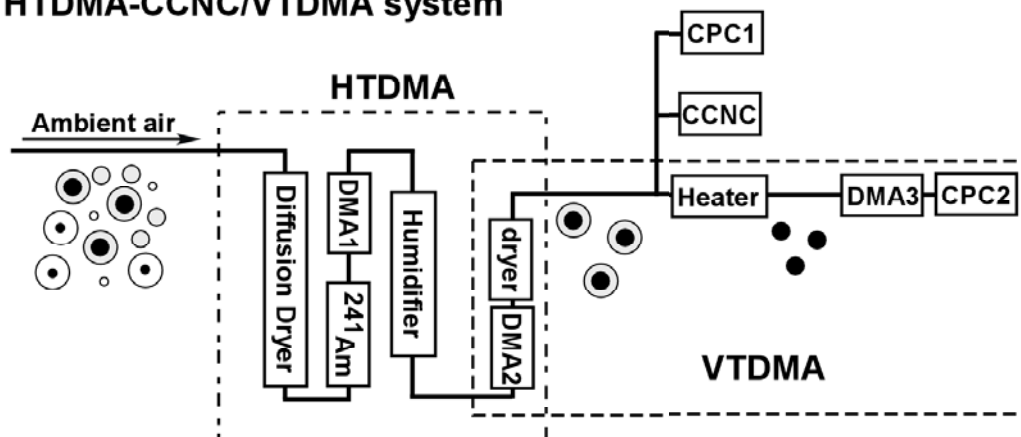


Figure 1

a) HTDMA-CCNC/VTDMA system



b) Thermodenuder TDMA system



Figure 2

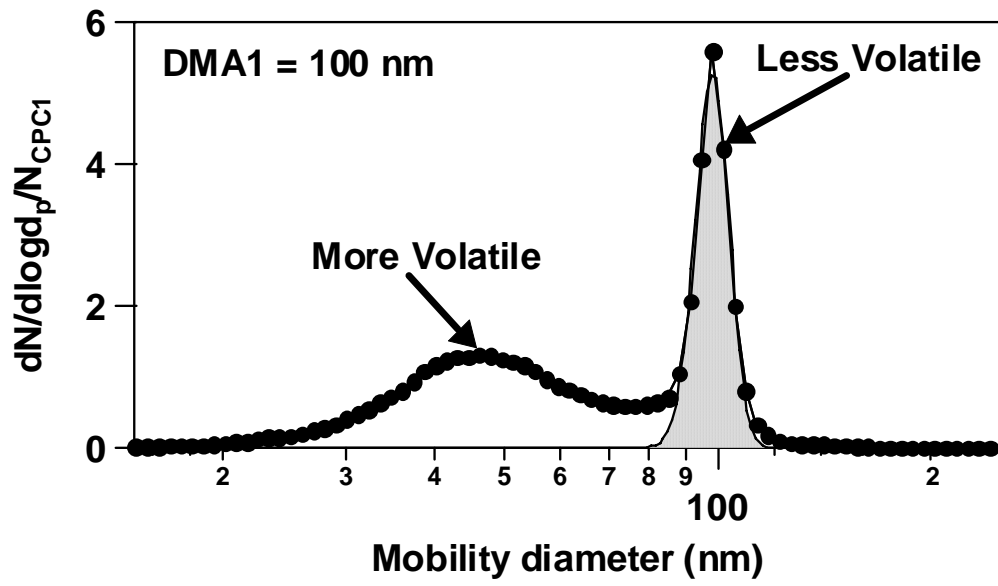


Figure 3

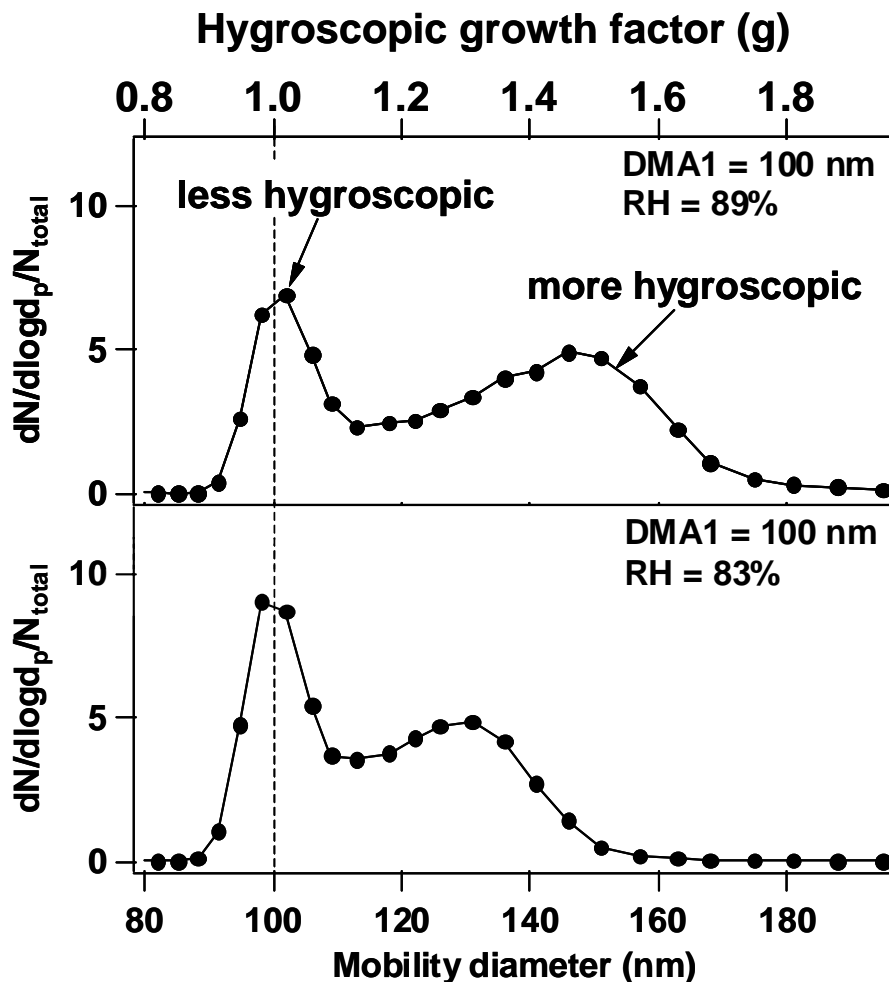


Figure 4

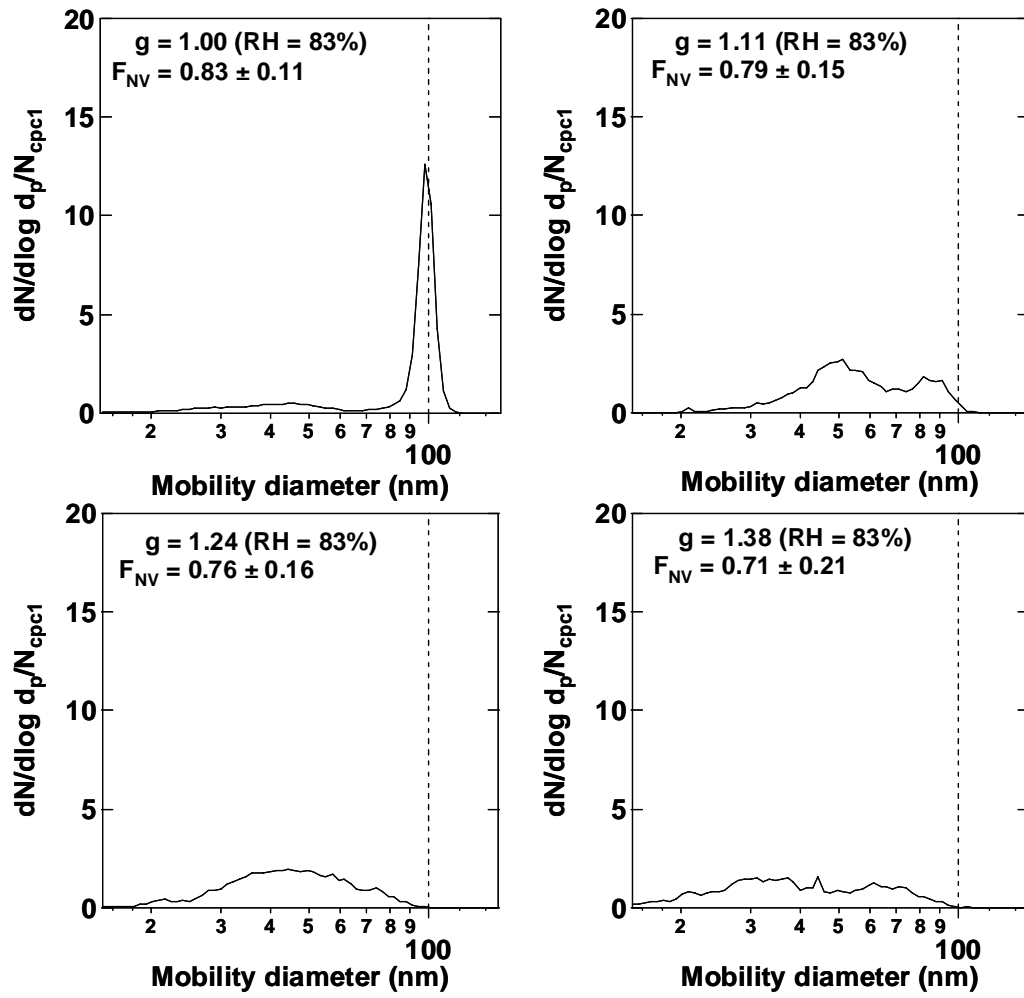


Figure 5

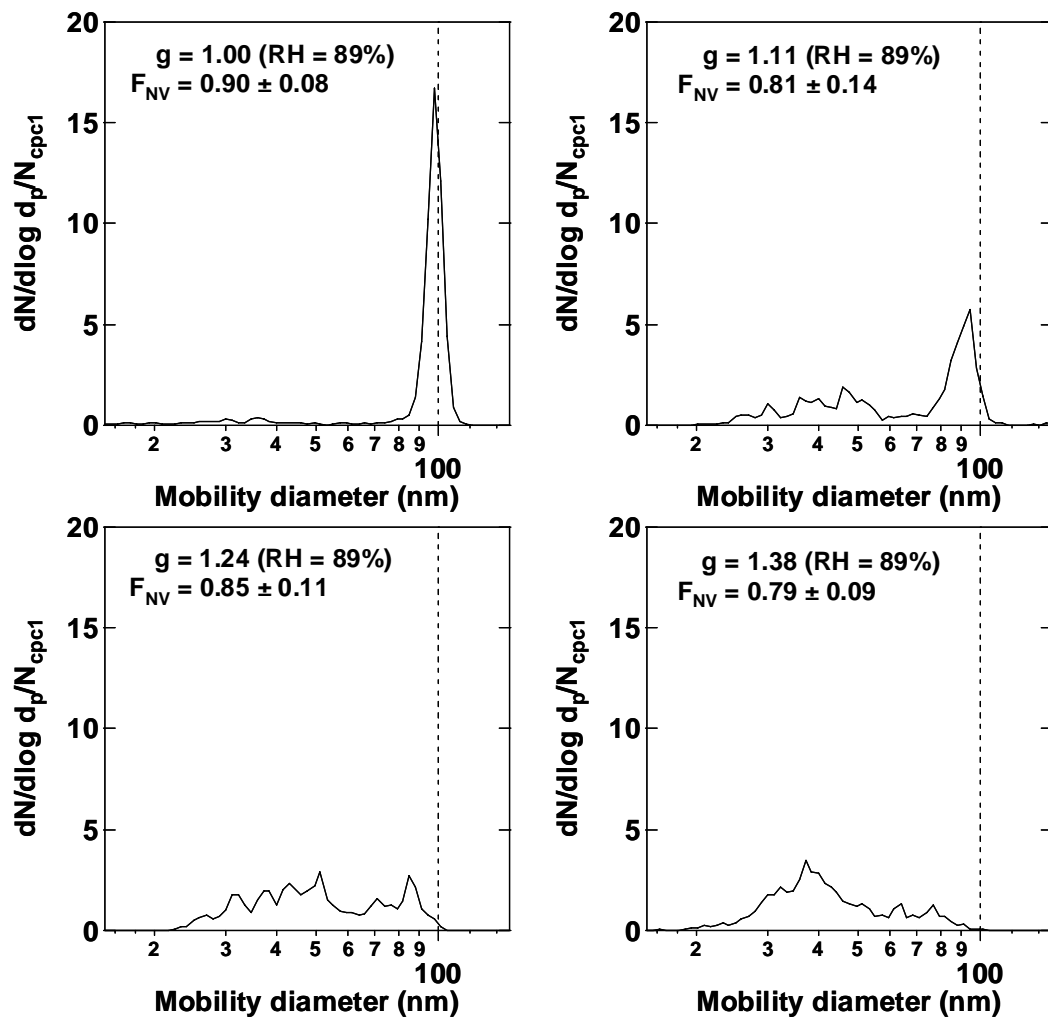


Figure 5 (continued)

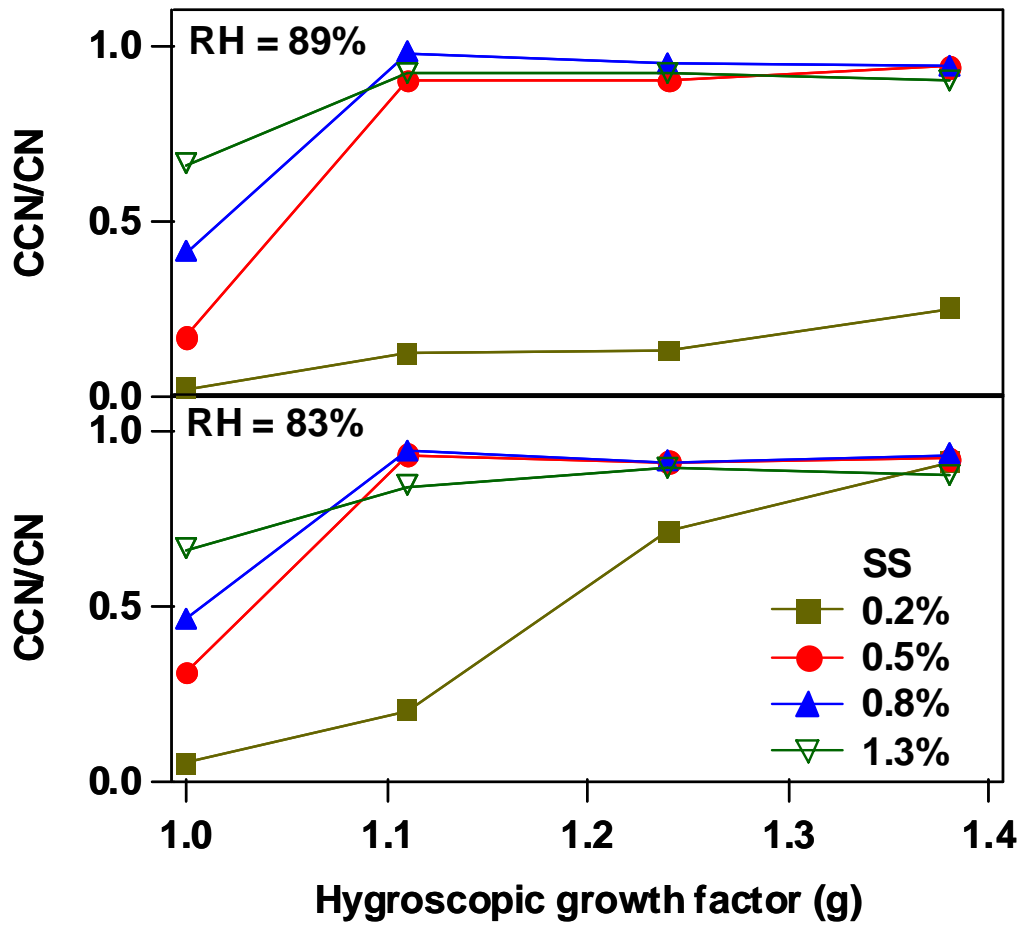


Figure 6

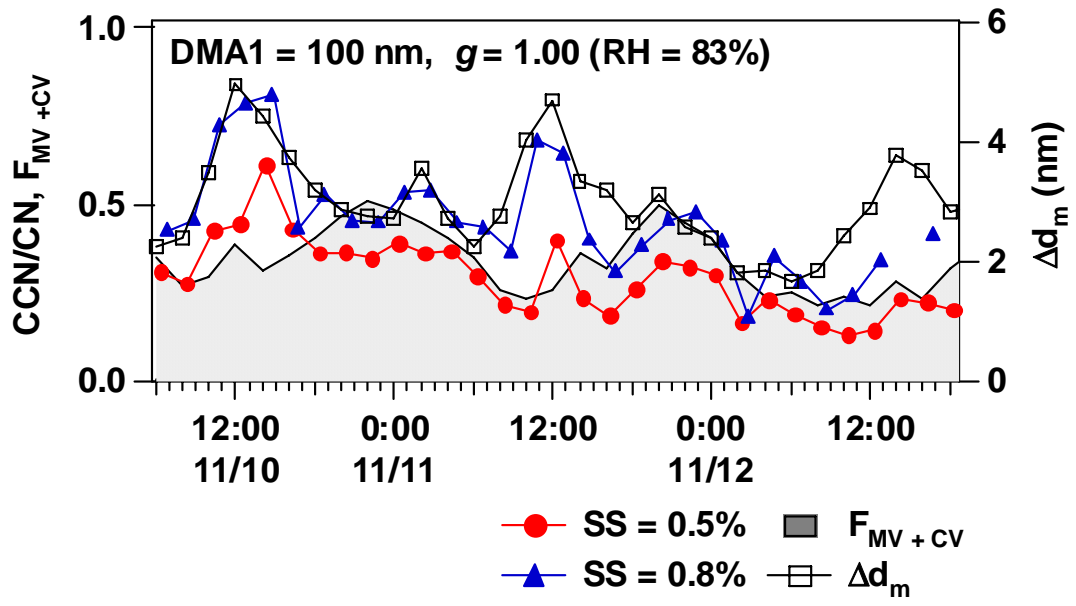


Figure 7

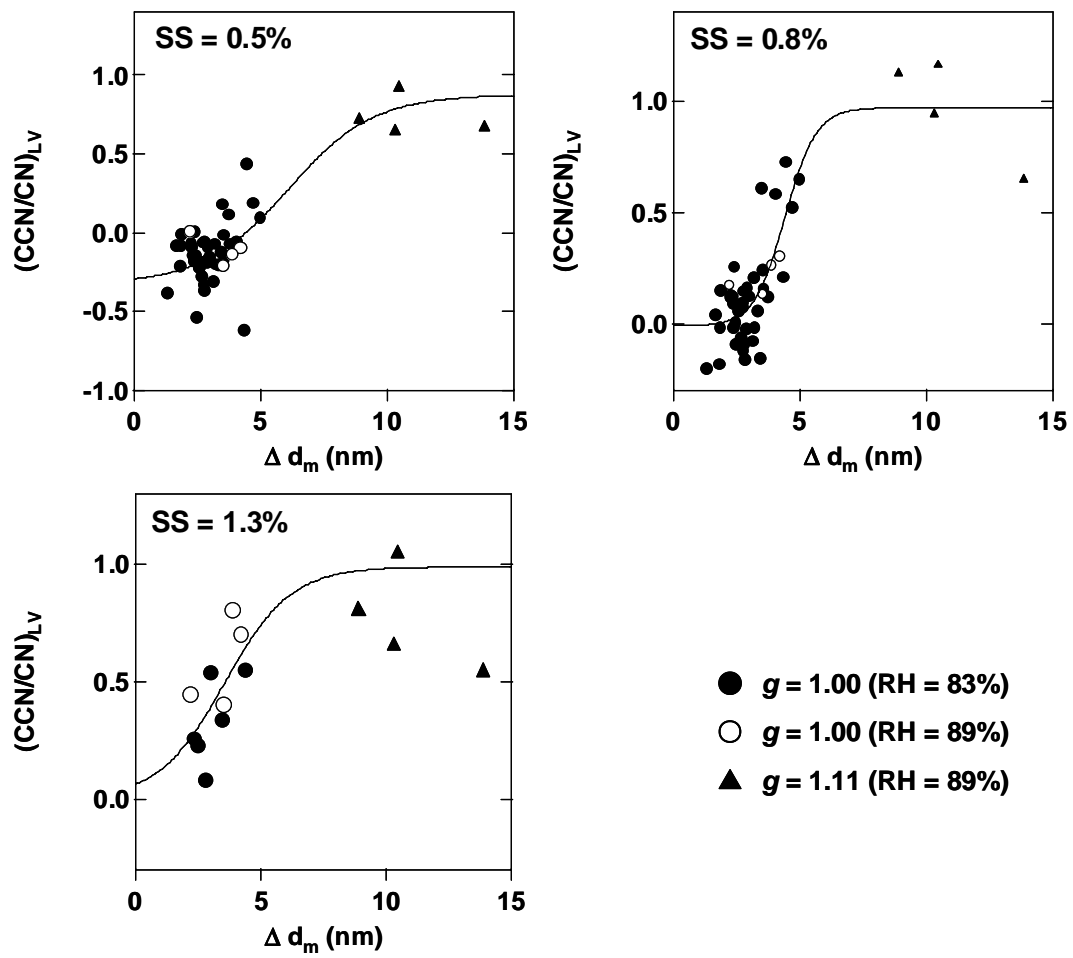


Figure 8

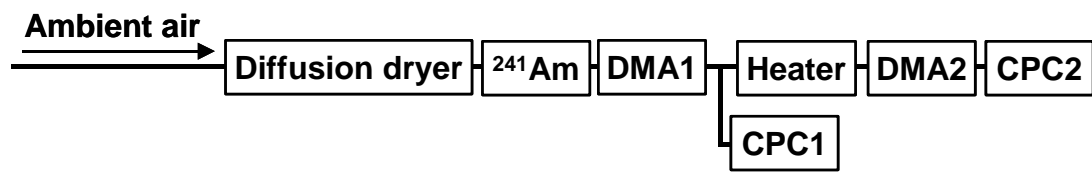


Figure A1