

CCN activity at Jeju  
Island, 2005

M. Kuwata et al.

# Cloud condensation nuclei activity at Jeju Island, Korea in spring 2005

M. Kuwata<sup>1</sup>, Y. Kondo<sup>1</sup>, Y. Miyazaki<sup>1</sup>, Y. Komazaki<sup>1</sup>, J. H. Kim<sup>2</sup>, S. S. Yum<sup>2</sup>,  
H. Tanimoto<sup>3</sup>, and H. Matsueda<sup>4</sup>

<sup>1</sup>Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan

<sup>2</sup>Department of Atmospheric Science, Yonsei University, Seoul, Korea

<sup>3</sup>Atmospheric Environmental Div., National Inst. for Environmental Studies, Tsukuba, Japan

<sup>4</sup>Geochemical Research Department, Meteorological Research Institute, Tsukuba, Japan

Received: 12 October 2007 – Accepted: 1 November 2007 – Published: 13 November 2007

Correspondence to: M. Kuwata (kuwata@atmos.rcast.u-tokyo.ac.jp)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

## Abstract

We measured the number concentrations of cloud condensation nuclei (CCN) and the size distributions of CCN/CN (CN: condensation nuclei) ratios at supersaturations (SSs) of 0.097, 0.27, 0.58, and 0.97% at Jeju-Island, Korea during March-April 2005.

5 Measurements of aerosol inorganic ions, water-soluble organic carbon (WSOC), organic carbon (OC), and elemental carbon (EC) in PM<sub>2.5</sub> were simultaneously made. The CCN/CN ratios increased with increasing particle diameter, and the diameter at CCN/CN=0.5 was defined as  $D_{50}$ .  $D_{50}$  represents the activation dry diameter of atmospheric particles. The average  $D_{50}$  at SS=0.097% and 0.97% was 136 nm and 31 nm, respectively. The temporal variation of  $D_{50}$  at SS=0.097% was correlated with the mass fraction of water-soluble components (inorganic ions + WSOC), indicating that the temporal variation of CCN activity was mainly controlled by changes in the water-soluble components fraction. The critical dry diameter ( $D_{crit}$ ), which is the threshold dry diameter for CCN activation, was calculated from the observed aerosol chemical compositions by Köhler theory for comparison with  $D_{50}$ . The  $D_{50}$  at SS=0.097% was correlated ( $r^2=0.48$ ) with calculated  $D_{crit}$ , although  $D_{crit}$  were larger than  $D_{50}$  by 20–29% on average. The systematic difference between  $D_{50}$  and  $D_{crit}$  could be caused by the size dependence of the aerosol chemical compositions or surface tension lowering caused by the mixing of water-soluble organic compounds. This difference corresponds to a  
20 27±14% uncertainty in the CCN number concentration estimated from the observed particle number size distribution.

## 1 Introduction

A subset of atmospheric particles acts as cloud condensation nuclei (CCN). An increase in CCN number concentration causes an increase in cloud droplet concentration and a decrease in droplet size, which in turn impacts cloud albedo and precipitation. Consequently, CCN can significantly influence climate through cloud processes  
25

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(Twomey, 1974; Lohmann and Feichter, 2005, and references therein).

The number concentration of CCN is determined by the number concentration of aerosol particles and the fraction of CCN active particles. This fraction is often denoted as the CCN/CN ratio because condensation nuclei (CN) counters have been used for total particle number concentration measurements (Seinfeld and Pandis, 2006). CCN/CN strongly depends on the size and chemical composition of aerosols. The influence of aerosol chemical composition and number size distribution on the bulk (size-unresolved) CCN/CN can be separated by measuring CCN/CN for size-selected particles. In particular, when aerosol particles are internally mixed, we can determine the threshold diameter from the measurements (Dusek et al., 2006). The threshold diameter can also be calculated by Köhler theory. Many laboratory studies have measured CCN/CN ratios of size-selected particles for comparison with theoretical calculations (e.g. Corrigan and Novakov, 1999; Raymond and Pandis, 2002). These experiments have shown that size-resolved CCN/CN ratios of laboratory-generated particles can be explained by Köhler theory. However, only a few studies have employed this measurement method for atmospheric observations (e.g. Dusek et al., 2006), leading to an insufficient understanding of controlling factors for the CCN activation of atmospheric particles.

CCN concentrations are often influenced by anthropogenic particles (Twomey, 1974; Hudson and Yum, 2002). In recent years, anthropogenic emission of aerosol precursors (e.g., SO<sub>2</sub> and NO<sub>x</sub>) from Asia has increased significantly (Streets et al., 2000; Akimoto et al., 2003; Richter et al., 2005). Remote sensing studies have indicated that the aerosol particles derived from anthropogenic pollutants from Asia have changed cloud radiative properties such as optical depth in this region (Chameides et al., 2002; Kawamoto et al., 2006). Thus, it is important to study CCN activity in this region for a more accurate assessment of the impact of anthropogenic aerosol on climate. However, only a few CCN studies have been performed in this region (e.g. Matsumoto et al., 1997; Yum et al., 2005), and the size resolved CCN/CN ratios have not been measured so far.

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

In this study, we have measured size-resolved CCN/CN ratios and CCN number concentrations at Gosan, Jeju Island, Korea, in March and April 2005 during the United Nations Environmental Programme (UNEP) Atmospheric Brown Cloud – East Asian Regional Experiment 2005 (ABC-EAREX2005) campaign. In addition to the CCN measurements, aerosol chemical composition was simultaneously observed. Observed threshold diameters for CCN activation are compared with the mass fractions of aerosol chemical compositions. Threshold diameters for the activation ( $D_{\text{crit}}$ ) are calculated and compared with the observed threshold diameter to investigate the controlling factors of  $D_{\text{crit}}$ .

## 2 Theory

The equilibrium water vapor pressure ( $S$ ) of an aerosol particle can be calculated by Köhler theory. According to the theory,  $S$  is described as follows (e.g., Roberts et al., 2002; Mochida et al., 2006):

$$\ln S = \frac{A}{d_{\text{wet}}} - \frac{Bd_{\text{dry}}^3}{(d_{\text{wet}}^3 - d_{\text{dry}}^3)} \quad \left( A = \frac{4M_w\sigma}{RT\rho_w} \quad B = \frac{M_w}{\rho_w} \frac{\sum_i \frac{\nu_i\phi_i\varepsilon_i m_i}{M_i}}{\sum_i \frac{m_i}{\rho_i}} \right) \quad (1)$$

where  $d_{\text{dry}}$  is the dry diameter of a particle and  $d_{\text{wet}}$  is the diameter of a droplet under equilibrium conditions. The suffix  $i$  denotes the properties of the  $i$ -th solute compound.  $M_w$  is the molecular weight of water;  $M_i$  is the molecular weight of solute;  $\rho_w$  is the density of water;  $\rho_i$  is density of solute;  $\sigma$  is the surface tension;  $R$  is the gas constant;  $T$  is the temperature;  $\nu_i$  is the stoichiometric number of ions and molecule;  $\phi_i$  is the osmotic coefficient;  $\varepsilon_i$  is the degree of dissolution; and  $m_i$  is the mass mixing ratio of the  $i$ -th solute. The first term on the right-hand side represents an increase in the equilibrium vapor pressure of water due to surface tension (the Kelvin effect). The second term on the right-hand side denotes the decrease in the equilibrium vapor

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

pressure of water because of solute mixing (Raoult's effect). When we consider  $S$  for an aerosol particle, it has a maximum value at a certain  $d_{\text{wet}}$  (critical droplet diameter). The supersaturation ( $SS$ :  $SS=S-1$ ) that corresponds to this  $S$  is called the critical supersaturation ( $SS_c$ ). Particles can grow to cloud droplets if the  $SS$  of the environment is higher than their  $SS_c$ .

If we assume that  $A$  and  $B$  are constants and  $d_{\text{wet}}$  is much larger than  $d_{\text{dry}}$ ,  $SS_c$  can be expressed as follows:

$$\ln(1 + SS_c) = \sqrt{\frac{4A^3}{27Bd_{\text{dry}}^3}} \quad (2)$$

This equation shows that  $SS_c$  decreases with particle diameters. Thus, at a certain  $SS$ , there exists a threshold value of  $d_{\text{dry}}$  above which all aerosol particles act as CCN. We denote this diameter as the critical dry diameter ( $D_{\text{crit}}$ ).

### 3 Experiment

#### 3.1 CCN measurement

Figure 1 shows the CCN observation system used for this study. In this system, ambient particles were dried to a relative humidity (RH) <5% using two diffusion dryers in series (TSI Model 3062). Dried particles were charged with a  $^{241}\text{Am}$  bipolar neutralizer. Particles were then introduced to a differential mobility analyzer (DMA: TSI Model 3081). The DMA classified particles by their electrical mobility. The voltage applied to the DMA was scanned stepwise to change the diameter of the classified particle (Table 1). The sheath to sample flow ratio of the DMA was set to 10:1. Classified particles were introduced to a condensation particle counter (CPC: TSI Model 3022) and a cloud condensation nuclei counter (CCNC: Droplet Measurement Technologies, Inc.) (Roberts and Nenes, 2005). The CPC monitored the number concentrations of

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

condensation nuclei (CN), and the CCNC measured number concentrations of CCN. The sample flow rate of the CCNC was set to 0.045 l/min, and the sheath flow rate was set to 0.455 l/min. The temperature gradient ( $\Delta T$ ) of the thermal gradient chamber in the CCNC was changed periodically to alter the SS in the chamber. Four  $\Delta T$ s (3.08, 4.62, 9.24 and 15.4 K) were used in this study. SSs corresponding to these  $\Delta T$ s were calibrated with ammonium sulfate particles as described by Kuwata et al. (2007). The calibration was performed at the observation site before and after the campaign. There are several different methods for the calculation of the water activity of ammonium sulfate particles (Kreidenweis et al., 2005, and references therein). We chose the ideal solution approximation ( $\phi=1$ ) in calculating the  $D_{\text{crit}}$  of atmospheric particles (Sect. 5). Therefore we used this approximation for the interpretation of the calibration results to ensure consistency. For comparison, SSs calculated using the osmotic coefficient of Clegg et al. (1996) are also shown in parentheses in Table 1. The differences of these two values give a measure of the uncertainty in the estimation of the SS in the CCN counter. The Debye – Hückel constant is needed to calculate the osmotic coefficient of Clegg et al. (1996) because it is based on the Pitzer model. The Debye – Hückel constant at 300 K was calculated by the equation given by Clegg et al. (1994).

Multiply charged particles were included in the classified particles, therefore an inverse analysis was performed for CCN and CN size distribution data for multiple-charge correction. The STWOM algorithm (Markowski, 1987) was used to obtain size distributions of CN and CCN. In this calculation, the equilibrium charge distribution (Wiedensohler, 1988) and the DMA transfer function derived by Knutson and Whitby (1975) were included in the kernel function. The raw data for CN and CCN were linearly interpolated so that the interval of each bin was  $\Delta \log d_p = 0.015$ . Size-resolved CCN/CN ratios were calculated using the data after the inverse analysis.

The three-way valve in Fig. 1 was switched once every 30 min for the direct measurement of the CCN number concentration in ambient air. It took 30 min for the measurement at each SS and 2 h were required for the entire measurement cycle.

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## 3.2 Measurements of aerosol composition, size distribution

Inorganic components ( $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) were measured by a particle-into-liquid sampler combined with ion chromatography (PILS-IC) (Orsini et al., 2003; Takegawa et al., 2005). The concentration of water-soluble organic carbon (WSOC) was measured by PILS combined with a total organic carbon analyzer (PILS-WSOC) (Sullivan et al., 2004; Miyazaki et al., 2006, 2007). Elemental carbon (EC) and organic carbon (OC) were measured by a semi-continuous thermal-optical carbon aerosol analyzer (Sunset Laboratory, Inc.) (Bae et al., 2004; Kondo et al., 2006; Miyazaki et al., 2006).  $\text{PM}_{2.5}$  cyclones were used for these instruments. The detection limits of the PILS-IC, PILS-WSOC, OC, and EC were estimated to be  $0.01 \mu\text{g}/\text{m}^3$ ,  $0.1 \mu\text{g}/\text{m}^3$ ,  $1.0 \mu\text{g}/\text{m}^3$ , and  $0.2 \mu\text{g}/\text{m}^3$ , respectively (Takegawa et al., 2005; Kondo et al., 2006; Miyazaki et al., 2006).

Aerosol number size distribution (10–300 nm) was measured with a scanning mobility particle sizer (SMPS 3936, TSI). The SMPS used in this study comprised a DMA (TSI Model 3081) and a CPC (TSI Model 3010). In addition, number concentration of particles larger than 10 nm (CN) was measured by another CPC (TSI Model 3010) (Yum et al., 2007). The concentration of carbon monoxide (CO) was measured using a non-dispersive infrared analyzer (Horiba APMA-360 model) (Sawa et al., 2007).

## 3.3 Measurement site

The observations were performed between 18 March and 5 April 2005 at Gosan ( $33.2^\circ \text{N}$ ,  $126.1^\circ \text{E}$ ) on Jeju Island, Korea, as part of the Atmospheric Brown Cloud – East Asian Regional Experiment 2005 campaign. The location of Gosan is shown in Fig. 2. The instruments were placed in a container located about 10 m back from the edge of a cliff. The sampling inlets were made of stainless steel tubes with an inner diameter of 7 mm. The top of the inlets was located about 4 m above the ground level.

The meteorological parameters at the Gosan site were observed by Korean Meteorological Administration (KMA). During the observation period, the dominant winds

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

were northerlies and north-northwesterlies (more than 50% of the observation period) associated with the Siberian high-pressure system. This led to the frequent transport of anthropogenic pollutants from the Korean Peninsula and China to Gosan. Sawa et al. (2007) attributed the high concentrations of CO at Gosan to the emissions from these regions using a chemical transport model. More detailed description of the meteorological conditions and the transport of anthropogenic pollutants can be found elsewhere (Sawa et al., 2007; Miyazaki et al., 2007). Previous studies have also shown that air masses observed at Gosan are heavily influenced by anthropogenic emissions from East Asia (Carmichael et al., 1997; Lee et al., 2006).

## 4 Results

### 4.1 CCN/CN size distributions

Figure 3 shows the average size-resolved CCN/CN ratio at  $SS=0.097\%$ , together with the data on specific days. The CCN/CN size distribution of ammonium sulfate obtained during calibration at the observation site (closed circles) is also shown in this figure for comparison. In general, CCN/CN increases with increasing diameter. At 02:00–02:30 on 26 March, the CCN/CN size distribution of ambient particles was very similar to that of ammonium sulfate, indicating that almost all particles were composed of ammonium sulfate at that time. On the other hand, on 28 March, the CCN/CN size distribution shifted to a larger diameter, and the rate of increase was lower than ammonium sulfate. This shift indicates that the bulk aerosol chemical composition on 28 March was significantly different from ammonium sulfate. The slower increase rate indicates the co-existence of different types of aerosol particles with different activation curves. This can be interpreted as co-existence of aerosol particles with different chemical composition considering that each activation curve depends on the chemical composition composing each type of particles.

We defined the threshold diameter for CCN activation to compare it with the mass

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



fraction of chemical compounds and theoretically calculated  $D_{\text{crit}}$ . In this study, the threshold diameter was defined as the diameter corresponding to  $\text{CCN}/\text{CN}=0.5$  ( $D_{50}$ ) because it represents the bulk chemical composition. If aerosol particles were not fully activated,  $D_{50}$  would not necessary corresponds to the threshold diameter. In all cases shown in Fig. 3, the  $\text{CCN}/\text{CN}$  ratios exceeded 0.85 at 250 nm. This suggests the appropriateness of the use of  $D_{50}$ .

## 4.2 Temporal variation of CCN and particle number size distribution

### 4.2.1 CCN number concentration

Figure 4a shows the time series of the CCN number concentration. In general, the variation in the CCN number concentration correlated with that of CO concentration (Fig. 4d). In particular, this correlation is clearly observed at  $SS=0.097\%$  ( $r^2=0.74$ ). Sawa et al. (2007) have reported high CO concentration between 22–24 March and 30 March–2 April due to transport of CO from the Korean Peninsula and China. During these periods, CCN concentration also increased (Figs. 4a and d). Thus, these high CCN concentrations were likely caused by the enhanced concentrations of anthropogenic aerosols transported from these regions. The average values and standard deviations of CCN number concentration are shown in Table 2. The average CCN number concentration at  $SS=0.097\%$  and  $0.97\%$  were  $1200\text{ cm}^{-3}$  and  $4000\text{ cm}^{-3}$ , respectively. These concentrations are higher than those of other remote areas of the world such as the Island of Tasmania in Australia and Mace Head in Ireland by about an order of magnitude (Covert et al., 1998; Reade et al., 2006). CCN concentrations measured at Gosan during this observation period were extensively compared with those obtained in other regions by Yum et al. (2007). The CCN concentrations observed in this study are close to those of Anmyeon (Korea: see Fig. 2) in springtime of 2004 ( $SS=1\%$ ) (Yum et al., 2005).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## 4.2.2 $D_{50}$

Figure 4b shows the time series of the number size distribution of aerosol particles and  $D_{50}$ . The  $D_{crit}$  of ammonium sulfate at each  $SS$  is also shown as dashed lines in this figure. The average values of  $D_{50}$  at  $SS=0.097\%$  and  $0.97\%$  were 136 nm and 31 nm, respectively (Table 2). In general, the  $D_{50}$  is almost equal to or slightly larger (by  $\sim 25\%$ ) than the  $D_{crit}$  of ammonium sulfate (125 nm and 27 nm, respectively). This means that the  $D_{crit}$  of ammonium sulfate is the smallest  $D_{crit}$  of the atmospheric particles during the observation period.

The temporal variation of  $D_{50}$  at different  $SS$ s did not always correlate. As shown in Eq. (2), the threshold diameter for CCN activation depends on  $A$  and  $B$ , which are determined by the aerosol chemical compositions. Thus, this difference in the temporal variations of  $D_{50}$  at each  $SS$  indicates the difference in temporal variation of chemical composition in different size ranges.

Using Eq. (2), we calculated  $B$  assuming the surface tension of water. This parameter gives information on the chemical composition (approximate number of solute ions and molecules included in a unit volume) at  $D_{50}$  of each  $SS$ . The results are summarized in Table 2. The average values of  $B$  did not depend on  $SS$  significantly, indicating that the chemical composition averaged over the observation period was rather uniform in the diameter range considered (30 to 160 nm).

## 4.2.3 Number size distribution

New particle formation events can have significant impact on CCN number concentration (e.g., O'Dowd et al., 2002; Laaksonen et al., 2005) and aerosol hygroscopicity, which is closely related to CCN activity (Buzorius et al., 2004). However, there has been no clear observational evidence of this effect. In Fig. 4b, new particle formation is clearly identified on 19, 25, 29, 30, and 31 March. It can be seen more clearly in Fig. 4c, which shows particle number concentration measured by CPC and CCN number concentration ( $SS=0.97\%$ ). Concentration of CCN ( $SS=0.97\%$ ) is a good indicator

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

of particle number concentrations larger than 30 nm. Thus, the difference of the number concentrations (CN–CCN ( $SS=0.97\%$ )) represents the number concentration of particles between 10 and 30 nm. During the periods of new particle formation events described above, the enhancement of number concentration of small (10–30 nm) particles was observed. In particular, the events occurring on 29 and 30 March were important in that newly formed particles influenced the CCN number concentration as a consequence of particle growth beyond  $D_{50}$ . Figure 5a and b show the CCN number concentrations, particle size distributions, and  $D_{50}$  during this event. The peak diameter of the size distribution obtained by bimodal lognormal fitting is shown as red lines in Fig. 5b.

At 14:00 local time (LT) on 29 March, small (<20-nm) particles appeared and began to grow. The peak diameter grew to 25 nm by 18:00 LT, and some particles grew larger than the  $D_{50}$  at  $SS=0.97\%$  (28 nm). At this time, the CCN number concentration ( $SS=0.97\%$ ) began to increase. The peak diameter and  $D_{50}$  ( $SS=0.97\%$ ) were equal at 21:00 LT (blue dashed vertical line in Fig. 5b). At this time, the majority of newly formed particles began to act as CCN at  $SS=0.97\%$ . In the case of  $SS=0.58\%$ , the peak diameter equaled  $D_{50}$  at 02:00 LT on 30 March, and the CCN number concentration increased from  $1700\text{ cm}^{-3}$  (01:30 LT) to  $5800\text{ cm}^{-3}$  (11:30 LT). At 03:00 LT, some portion of the particles grew large enough to act as CCN at  $SS=0.27\%$ . Then, CCN number concentration at  $SS=0.27\%$  increased from 1000 to  $4700\text{ cm}^{-3}$  with the increase in the peak diameter. For this  $SS$ , the peak diameter reached  $D_{50}$  at 10:00 LT. At the same time, another new particle formation event occurred, and this event also clearly affected the CCN number concentration at  $SS=0.97\%$  and  $0.58\%$ . At 12:00 LT, some fraction of the particles grew larger than the  $D_{50}$  at  $SS=0.097\%$ , and they affected the CCN number concentration at this  $SS$ . A similar phenomenon was also observed on 25 March (Figs. 4a and b). These results clearly show that the newly formed particles significantly increased the CCN number concentration.

Buzorius et al. (2004) have shown that the deliquescence relative humidity and the hygroscopic growth of newly formed particles at Gosan during ACE-Asia campaign

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

were similar to those of ammonium sulfate. In the present study, the observed  $D_{50}$  of newly formed particles was also similar to ammonium sulfate. For instance, the  $D_{50}$  of  $SS=0.97\%$  was 27 nm at 21:00 LT, 29 March, and that of  $SS=0.27\%$  was 66 nm at 10:00 LT, 30 March. The  $D_{crit}$  of ammonium sulfate was 27 nm and 63 nm, respectively (Table 1). This result indicates that newly formed particles observed in this event were mainly composed of inorganic compounds such as ammonium sulfate, consistent with Buzorius et al. (2004).

Previous studies have suggested that new particle formation has an impact on the CCN number concentration from the measurements of number size distributions (e.g., O'Dowd et al., 2002; Laaksonen et al., 2005) and modeling (e.g., Arnold, 2006; Sotiropoulou et al., 2006). The present observations clearly demonstrate that new particle formation is one of the important processes of CCN formation at Gosan.

Figure 6 shows the number size distribution of all particles and CCN averaged over the whole observation period. Averaged CCN/CN ratios were multiplied by the number size distribution measured by the SMPS averaged over the observation period to obtain the rough estimate of the CCN size distribution. The peak diameter of the average CCN size distribution was about 150 nm at  $SS=0.097\%$  and shifted to about 80 nm at  $SS=0.97\%$ . Detailed discussion of number size distribution of particles during the observation period has been given by Yum et al. (2007).

#### 4.3 Ion balance of inorganic components

The average concentrations of the inorganic components measured by PILS-IC are summarized in Table 3.  $NH_4^+$  was the most abundant cation (56%), and  $Ca^{2+}$  was the second (15%).  $SO_4^{2-}$  was the most abundant anion (67%). Topping et al. (2004) measured inorganic components using a Berner impactor at Gosan during the ACE-Asia campaign. They showed that the concentration of  $NH_4^+$  was the highest at the 0.2–0.5  $\mu m$  stage, and  $Ca^{2+}$  was the highest at the 1.5–5.5  $\mu m$  stage. In this study, the  $D_{50}$  values were in the sub-micrometer range (Fig. 4). Thus,  $Ca^{2+}$  was ignored in

the following discussion of CCN activity.  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$  were also ignored for the same reason.

Figure 7 shows the ion balance of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ . The cation and anions balance very well (slope = 0.94). This result shows that sulfate and nitrate in  $\text{PM}_{2.5}$  were neutralized by ammonium at Gosan. The addition of  $\text{K}^+$  to the ion balance causes the balance to deviate from the 1:1 line. This suggests that neither  $\text{NO}_3^-$  nor  $\text{SO}_4^{2-}$  were the counter ions of  $\text{K}^+$ . In addition, because the molar concentration of  $\text{K}^+$  was only 8% of  $\text{NH}_4^+$ , we ignored  $\text{K}^+$ . In the following discussion, we assume that the inorganic component of sub-micron particles was composed only of ammonium sulfate and ammonium nitrate.

## 5 Discussion

### 5.1 Temporal variation of $D_{50}$ and aerosol composition

Figure 8 shows the temporal variation of  $D_{50}$  ( $SS=0.097\%$ ) and the mass fraction of the aerosol components. In this figure, the aerosol components were divided into four groups: inorganic ( $\text{NH}_4^+ + \text{SO}_4^{2-} + \text{NO}_3^-$ ), WSOC, water-insoluble organic carbon ( $\text{WIOC} = \text{OC} - \text{WSOC}$ ), and EC. Inorganic components and WSOC are soluble in water, while WIOC and EC are insoluble in water. Note that the masses of WSOC and WIOC are the masses of carbon in organic compounds and do not include the masses of other elements (e.g., oxygen and hydrogen) (Kondo et al., 2007). The temporal variation of  $D_{50}$  and the water-soluble fraction (inorganic + WSOC) are correlated. With the increase in the water-soluble fraction,  $D_{50}$  decreases. This is consistent with Köhler theory because the value of  $B$  in Eq. (2) increases with the increase of the water-soluble fraction. This good correlation indicates that the variation of  $D_{50}$  was not significantly influenced by the variation in the chemical composition of the water-soluble component (e.g., change of inorganic/WSOC ratio). Kim et al. (2006) have shown that the hygroscopicity of aerosol particles at Gosan was correlated with the mass fraction of

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

sulfate. This indicates that  $B$  is mainly determined by inorganic components because hygroscopicity is mainly determined by  $B$  (e.g., Kreidenweis et al., 2005; Mochida et al., 2006). This is consistent with the present observations because the mass fraction of inorganic compounds was significantly larger than that of WSOC during this period (Fig. 8).

The  $D_{50}$  at  $SS=0.097\%$  did not necessarily correlate with those of higher  $SS$ s (Fig. 4b), as discussed in Sect. 4.2.2. Correlation of  $D_{50}$  at  $SS=0.097\%$  with those at higher  $SS$ s decreased with the increase in  $SS$  ( $r^2=0.25$  and  $0.00$  for  $SS=0.27\%$  and  $0.97\%$ , respectively). This indicates that the temporal variation of the mass fraction of  $PM_{2.5}$  was reflected in that of  $D_{50}$  at  $SS=0.097\%$  (100–200 nm) but was not reflected in  $D_{50}$  at higher  $SS$ s (<100 nm). This is because the contribution to the  $PM_{2.5}$  mass concentration of particles with diameters smaller than 100 nm was much smaller than that of 100–200 nm.

## 5.2 Comparison of $D_{50}$ and calculated $D_{crit}$

In this section, we compare the observed  $D_{50}$  and the  $D_{crit}$  calculated from the simultaneously measured chemical composition. We first discuss the assumptions used to calculate  $A$  and  $B$  in the Köhler theory (Sect. 2). The surface tension of water (72 mN/m) was assumed for the calculation of  $A$ . The calculation was performed at  $T=300$  K. For the calculation of  $B$ , the ideal solution approximation ( $\phi=1$ ) was used. We used the simultaneously measured aerosol chemical composition ( $PM_{2.5}$ ) assuming that chemical composition was not size-dependent. Assumptions regarding the chemical composition and chemical properties of organic compounds (e.g. molecular weight (MW), elemental ratio, density) are also required for the calculation of  $B$ . Kawamura et al. (2003) and Mochida et al. (2003) measured dicarboxylic acids and other water-soluble organic compounds over the Sea of Japan and Yellow Sea during the ACE-Asia campaign. The concentration of oxalic acid was higher than that of other compounds by an order of magnitude. Simoneit et al. (2004) also measured dicarboxylic acids at Gosan during ACE-Asia campaign. Adipic acid was the largest linear

### CCN activity at Jeju Island, 2005

M. Kuwata et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

molecule in MW among the dicarboxylic acids they measured. Oxalic acid has one of the smallest molecular weights among atmospheric aerosol organic compounds. Therefore, if we assume that all carbon atoms in WSOC originated from oxalic acid, we will estimate a maximum Raoult's effect. In this study, this assumption is called as "oxalic acid assumption." As an extreme case, we calculated the  $D_{\text{crit}}$  using this assumption. The average molecular weight of WSOC should be higher than that of oxalic acid because dicarboxylic acids and saccharides with larger molecular weights were also observed at Gosan (Simoneit et al., 2004). In fact, Miyazaki et al. (2007) indicated that a significant portion of WSOC measured during ABC-EAREX2005 campaign could be attributed to organic compounds having a MW larger than oxalic acid. To test the sensitivity of  $D_{\text{crit}}$  on the assumed WSOC composition, we also calculated  $D_{\text{crit}}$  assuming that the average properties (MW, elemental composition, and density) of water-soluble organic compounds are equal to that of adipic acid. In this study, this assumption is called the "adipic acid assumption." In addition, recent studies have shown that significant fractions (20–60%) of WSOC are high-molecular weight compounds such as humic-like substances (HULIS) (Graber and Rudich, 2006, and references therein). It will correspond to the lowest estimate of Raoult's effect to calculate  $D_{\text{crit}}$  under the assumption that all WSOC are originated from HULIS (HULIS assumption). As in other cases, we need chemical properties of HULIS for the calculation, although chemical properties of HULIS vary depending on samples used (Graber and Rudich, 2006). For this calculation, we assumed an elemental composition of HULIS of C:H:O=1:1.16:0.63 (Dinar et al., 2006a), a density of 1.5 g/cm<sup>3</sup> (Dinar et al., 2006b; Hoffer et al., 2006), and an averaged molecular weight of 700 Da (Dinar et al., 2006a). In these calculations, water-soluble organic compounds were assumed to be completely dissolved in water ( $\epsilon=1$ ).

The chemical properties of WIOC are also required for the calculation of  $B$ . Simoneit et al. (2004) have measured alkanes, fatty acids, and polycyclic aromatic hydrocarbons (PAHs) at Gosan. Among these compounds, the mass fractions of PAHs were very limited. Most of carbon atoms of alkanes and fatty acids are in methylene groups

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(-CH<sub>2</sub>-). Therefore, we assumed that all carbon atoms in WIOC originated from methylene groups. The density of WIOC was assumed to be 0.8 g/cm<sup>3</sup> because the densities of hydrocarbons and fatty acids are typically 0.7–0.9 g/cm<sup>3</sup> (Pang et al., 2006). The properties of EC were assumed to be equal to those of graphite. The values used for the calculation are summarized in Table 4.

The observed  $D_{50}$  and calculated  $D_{crit}$  at  $SS=0.097\%$  are compared in Fig. 9. This figure shows three calculated results based on the oxalic acid, adipic acid, and HULIS assumptions. In all cases, the temporal variations of the calculated  $D_{crit}$  correlated with the observed  $D_{50}$ . However, the calculated  $D_{crit}$  values are systematically larger than the observations by 20–29%.

The correlations of  $D_{50}$  and the calculated  $D_{crit}$  (adipic acid assumption) are shown in Fig. 10. At all  $SS$ s, the calculated diameters are larger than the observations. The differences between the calculated  $D_{crit}$  and the observed  $D_{50}$  (calc – obs) are summarized in Table 5. In all cases,  $D_{crit}$  was overestimated by 16–29%.

The  $r^2$  values decrease with increasing  $SS$  (diminishing  $D_{50}$ ). This is likely due to the size dependence of the temporal variation of the aerosol chemical compositions as discussed in Sect. 4.2.2.

### 5.3 Possible causes of the discrepancy

In this section, we discuss the possible causes of the difference between  $D_{50}$  and  $D_{crit}$  and identify critical assumptions for the calculation of  $D_{crit}$ .

In calculating  $B$ , we assumed the composition and chemical properties of each component. The average chemical properties of water-soluble organic compounds were assumed to be identical to those of oxalic acid, adipic acid, or HULIS. Nevertheless, the  $D_{crit}$  values were larger than  $D_{50}$  even in the case of the oxalic acid assumption (the maximum estimation of  $B$ ). Therefore, the assumption on the chemical composition of WSOC is not the main cause of this discrepancy.

We assumed a density of 0.8 g/cm<sup>3</sup> for water insoluble organic compounds. If the actual density was larger than this value, this leads to the overestimation of  $D_{crit}$  be-

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



cause of the underestimation of  $B$  (Eq. 1). However, a sensitivity study of the density of WIOC (up to  $1.2 \text{ g/cm}^3$ ) under the oxalic acid assumption showed that calculated  $D_{\text{crit}}$  still overestimated the observations ( $D_{\text{crit}} - D_{50} = 20 \pm 12 \text{ nm}$  at  $SS = 0.097\%$ ).

The assumption of complete dissolution corresponds to the maximum estimation of  $B$  (minimum estimation of  $D_{\text{crit}}$ ). We used the ideal solution approximation in the calculation. If the discrepancy is due to this effect, the osmotic coefficient at the critical droplet diameters needs to be increased by a factor of about 2, considering the magnitude of the discrepancy (Table 5) and Eq. (2). Nevertheless, such a large change in the osmotic coefficients is unlikely, as the solution was very dilute at the critical droplet diameters.

In this study, the aerosol chemical composition was measured at  $\text{PM}_{2.5}$ . If the chemical compositions of  $\text{PM}_{2.5}$  do not represent those at  $D_{50}$  ( $< 200 \text{ nm}$ ), it causes an error in the calculation of  $D_{\text{crit}}$ . We discuss this point in detail in Sect. 5.3.1.

The surface tension of water was assumed for the calculation of  $A$  in Eq. (2). If the decrease in surface tension due to WSOC was significant, it may affect the  $D_{\text{crit}}$  (Facchini et al., 1999). This point is discussed in Sect. 5.3.2.

### 5.3.1 Size dependence of chemical composition

Some studies have used size-resolved aerosol chemical composition for CCN closure studies (e.g., Cantrell et al., 2001; Roberts et al., 2002). These studies have shown the size-dependence of aerosol chemical composition. In addition, Medina et al. (2007) have shown that the use of size-resolved chemical composition can decrease the error in the closure of the CCN number concentration. Topping et al. (2004) measured size-resolved chemical composition at Gosan during ACE-Asia campaign using a Berner impactor. They reported the size distribution of mass fractions of inorganic compounds and WSOC, and the results clearly showed the size-dependence. However, it is difficult to use their results to estimate the effect of size-dependent chemical composition because they did not measure water-insoluble components of the impactor samples. Mochida et al. (2007) have measured aerosol chemical compounds sampled with a

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Micro-Orifice Uniform Deposit Impactor (MOUDI) over the East China Sea and the Sea of Japan during ACE-Asia campaign. They found that the submicron mode was enriched by  $\text{nss-SO}_4^{2-}$  ( $[\text{OC}]/[\text{nss-SO}_4^{2-}] \approx 0.2$  at  $0.18\text{--}0.56\ \mu\text{m}$ ), whereas the supermicron mode was enriched by organic compounds ( $[\text{OC}]/[\text{nss-SO}_4^{2-}] \approx 1$  at  $1.8\text{--}5.6\ \mu\text{m}$ ). The median value of  $[\text{OC}]/[\text{SO}_4^{2-}]$  in the present study is 1.0, suggesting that  $\text{PM}_{2.5}$  chemical composition was affected by super-micron particles by comparison with the ratio of Mochida et al. (2007).

The  $D_{\text{crit}}$  for each SS was calculated using the chemical composition of the submicron mode particle given in Table 2 in Mochida et al. (2007) assuming that OC was entirely composed of WIOC because the fraction of WSOC was much smaller than that of WIOC (Fig. 8) and WSOC concentration was not reported. The major difference of this calculation is the higher sulfate fraction ( $[\text{OC}]/[\text{nss-SO}_4^{2-}] \approx 0.2$ ). At  $SS=0.097\%$ , the observed  $D_{50}$  was  $136 \pm 17\ \text{nm}$ , and the calculated  $D_{\text{crit}}$  using the data of Mochida et al. (2007) was  $142\ \text{nm}$ , as summarized in Table 6. In the case of other SSs, the  $D_{\text{crit}}$  also agree with the average value of  $D_{50}$ . This result shows possible effects of the size-dependent chemical composition on CCN activation.

The size dependence of aerosol chemical composition is clearer for the period of new particle formation. The  $D_{50}$  values of newly formed particles were very close to that of ammonium sulfate, as discussed in Sect. 4.2.3. In particular, newly formed particles grew larger than  $D_{50}$  at  $SS=0.097\%$  on 31 March (Fig. 4), and  $D_{50}$  values were nearly equal to the  $D_{\text{crit}}$  of ammonium sulfate on that day (Fig. 9). However, the mass fraction of carbonaceous aerosols (WSOC + WIOC + EC) at  $\text{PM}_{2.5}$  was about 30% at this time (Fig. 8), and this led to the overestimation of  $D_{\text{crit}}$  (Fig. 9). The decrease of  $D_{50}$  associated with new/secondary particle formation was also observed on 25 March. In this case, the mass fraction of water-insoluble compounds was also 30–40%, and this caused the overestimation of  $D_{\text{crit}}$ . These results suggest that the  $\text{PM}_{2.5}$  mass concentration was biased by large ( $>200\text{-nm}$ ) particles at least during these periods.

## CCN activity at Jeju Island, 2005

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

### 5.3.2 Decrease of surface tension by organic compounds

As described above, the surface tension of water was assumed for the calculation in this study. Nevertheless, if the decrease in surface tension due to organic compounds was significant, it may affect the critical  $SS$  of the particles (Facchini et al., 1999).

Surface tension lowering effects have been observed in various regions of the world such as Po Valley in Italy (Facchini et al., 1999), Mace Head in Ireland (Cavalli et al., 1999), and the Great Hungarian Plain (Kiss et al., 2005). In particular, Decesari et al. (2005) measured the surface tension lowering effect of aerosol, cloud water, and wet deposition samples at Jeju Island during the ACE-Asia campaign. They showed that the decrease of the surface tension due to aerosol was relatively small, whereas the surface tension decrease of cloud water and wet-deposition samples was significant. McFiggans et al. (2006) compared these results, and they showed that the magnitude of the effect for cloud water at Jeju Island was the most significant, and the effects for Po Valley and Mace Head samples were not as large as that of cloud water at Jeju (the red and blue lines in Fig. 11). They summarized the fitted parameters of Szyszkowski-Langmuir (Eq. 3) obtained for these observation results,

$$\sigma = \sigma_0 - bT \ln(1 + aC) \quad (3)$$

where  $\sigma_0$  is the surface tension of pure water,  $C$  is the WSOC concentration of the solution, and  $a$  and  $b$  are the empirical parameters obtained by fitting the observational results. In order to investigate the sensitivity of  $D_{\text{crit}}$  to surface tension, we calculated the  $D_{\text{crit}}$  at each  $SS$  using the parameters given by McFiggans et al. (2006). In this calculation, the adipic acid assumption was used, and the values for Jeju cloud water and Po Valley fog were employed. Substituting  $\sigma$  in Eq. (1) by that expressed by Eq. (3), the  $D_{\text{crit}}$  values were obtained by numerical calculation. The results are summarized in Fig. 12. In the case of Jeju cloud water, the calculated diameters for all  $SS$ s are smaller than the observed  $D_{50}$  by 10–47%, and the use of the equation for Po Valley decreased the differences between  $D_{\text{crit}}$  and  $D_{50}$  (7 to –13%). This indicates that the decrease of surface tension can potentially explain the discrepancy. The surface tension at the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

critical SS was about 46–56 mN/m (Jeju cloud water) and 51–62 mN/m (Po Valley), respectively (Fig. 11).

The discussion in this section and Sect. 5.3.1 shows that the size-dependence of chemical composition and the decrease in surface tension are the critical parameters in estimating  $D_{\text{crit}}$ . For a more quantitative assessment of these effects, we need simultaneous measurements of these parameters and  $D_{50}$ .

#### 5.4 Impact of $D_{\text{crit}}$ on CCN number concentration

The main purpose of the calculation of  $D_{\text{crit}}$  is the precise estimation of CCN number concentration from the particle size distribution. We estimated the difference in CCN number concentration due to the difference in  $D_{50}$  and calculated  $D_{\text{crit}}$ . The following equation was used for the assessment of the difference:

$$\frac{\Delta N_{\text{CCN}}}{N_{\text{CCN}}} = - \frac{\int_{\log(D_{50})}^{\log(D_{\text{crit}})} f_N(\log D_p) d \log D_p}{N_{\text{CCN}}} \quad (4)$$

where  $N_{\text{CCN}}$  is the number concentration of CCN measured by the CCN counter,  $\Delta N_{\text{CCN}}$  is the difference of the CCN number concentration caused by the error in the estimation of  $D_{\text{crit}}$ , and  $f_N(\log D_p)$  is the number size distribution measured by the SMPS. Therefore,  $\Delta N_{\text{CCN}}/N_{\text{CCN}}$  is the ratio of the difference of the CCN number concentration due to the difference in  $D_{\text{crit}}$  and the observed CCN number concentration.  $\Delta N_{\text{CCN}}/N_{\text{CCN}}$  depends on the number size distribution ( $f_N(\log D_p)$ ) and the uncertainty of the chemical composition ( $D_{\text{crit}}-D_{50}$ ). For this calculation, the calculated  $D_{\text{crit}}$  (adipic acid assumption, surface tension of water) was used. In addition to the adipic acid assumption, we also calculated  $\Delta N_{\text{CCN}}/N_{\text{CCN}}$  using the ammonium sulfate assumption ( $D_{\text{crit}}=D_{\text{crit}}$  of ammonium sulfate) because this assumption has frequently been used in previous CCN studies (e.g., VanReken et al., 2003), including those for Gosan (Yum et al., 2007).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

The results are summarized in Fig. 13. In general, the adipic acid approximation underestimates the CCN number concentration due to the overestimation of  $D_{\text{crit}}$ , whereas the ammonium sulfate approximation overestimates the CCN number concentration because of the underestimation of the  $D_{\text{crit}}$ . At  $SS=0.097\%$ ,  $\Delta N_{\text{CCN}}/N_{\text{CCN}}$  was  $-0.27\pm 0.14$  and  $0.16\pm 0.18$  for the adipic acid and ammonium sulfate approximations, respectively. These values give a measure of the uncertainty associated with the CCN prediction based on the results of this study. The absolute value of  $\Delta N_{\text{CCN}}/N_{\text{CCN}}$  increased with decreasing  $SS$ . During the observation period, the average values of  $B$  did not show a significant dependence on the value of  $SS$  as discussed in the Sect. 4.2.2, and the magnitude of error associated with the estimation of  $D_{\text{crit}}$  does not depend on  $SS$  significantly. Thus, this trend was not mainly due to the size dependence of the chemical composition.  $D_{\text{crit}}$  decreased with increasing  $SS$ . The particle number concentration between  $D_{50}$  and  $D_{\text{crit}}$  was smaller at higher  $SS$  in comparison with the CCN number concentration because at higher  $SS$ , a larger fraction of CCN is in the size range larger than  $D_{50}$ , as can be seen from Fig. 6. These results show that the effect of chemical composition on  $N_{\text{CCN}}$  was more important at lower  $SS$ , and the aerosol number size distribution was important for higher  $SS$ .

## 6 Summary

We measured the CCN number concentration ( $N_{\text{CCN}}$ ) and the size-resolved CCN/CN ratios at  $SS=0.097$ ,  $0.27$ ,  $0.58$ , and  $0.97\%$  on Jeju Island, Korea, during 18 March–5 April 2005. The average CCN number concentrations for the whole observational period were as high as  $1194\pm 746\text{ cm}^{-3}$  ( $SS=0.097\%$ ) and  $3966\pm 1686\text{ cm}^{-3}$  ( $SS=0.97\%$ ). The CCN/CN ratios monotonically increased with increasing particle diameter and the diameter at  $\text{CCN}/\text{CN}=0.5$  was defined as  $D_{50}$ . The average  $D_{50}$  values at  $SS=0.097\%$  and  $0.97\%$  were  $136\text{ nm}$  and  $31\text{ nm}$ , respectively. These values were slightly larger than those of ammonium sulfate particles ( $125$  and  $27\text{ nm}$  at  $SS=0.097\%$  and  $0.97\%$ , respectively). In particular,  $D_{50}$  diameters of newly formed

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

particles and those of ammonium sulfate particles were almost identical for  $SS=0.97$ , 0.58 and 0.27%, indicating that these particles were mainly composed of ammonium sulfate. The peak diameter of the CCN size distribution averaged for the whole observational period was about 150 nm at  $SS=0.097\%$  and shifted to about 80 nm at  $SS=0.97\%$ .

The temporal variation of  $D_{50}$  at  $SS=0.097\%$  was negatively correlated with the variation of the water-soluble fraction (inorganics + WSOC) of the aerosol components. For quantitative comparison, the threshold diameters for CCN activation ( $D_{crit}$ ) were calculated by Köhler theory assuming the surface tension of water and  $PM_{2.5}$  aerosol chemical composition. The calculated  $D_{crit}$  values were correlated with  $D_{50}$  at  $SS=0.097\%$  ( $r^2=0.48$ ). However,  $D_{crit}$  was systematically larger than  $D_{50}$  by about 16–29%. Sensitivity studies have shown that this discrepancy can be explained by possible differences in aerosol chemical composition between sub-micron and super-micron size ranges. In addition, a decrease of the surface tension due to the existence of WSOC can also significantly decrease  $D_{crit}$ .

The particle number concentrations in the size range between  $D_{50}$  and  $D_{crit}$  ( $\Delta N_{CCN}$ ) were calculated using the observed size distribution. The ratios of  $\Delta N_{CCN}$  to  $N_{CCN}$  ( $\Delta N_{CCN}/N_{CCN}$ ) were estimated to be  $-0.27\pm 0.14$  and  $-0.10\pm 0.13$  at  $SS=0.097\%$  and 0.97%, respectively, assuming that water-soluble organic compounds are represented by adipic acid. The  $\Delta N_{CCN}/N_{CCN}$  ratio gives a measure of the uncertainty in estimating CCN number concentrations using particle number size distributions and  $PM_{2.5}$  chemical compositions in the East Asia region.

*Acknowledgements.* We thank C. S. Hong and Y. J. Kim for their support of the observations. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), the Japanese Science and Technology Agency (JST), and the global environment research fund of the Japanese Ministry of the Environment. M. Kuwata thanks the Japan Society for the Promotion of Science (JSPS) for a JSPS Research Fellowship for Young Scientists. J. H. Kim and S. S. Yum were supported by the Korean Ministry of Environment under the “Eco-technopia 21 project”.

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## References

- Akimoto, H: Global air quality and pollution, *Science*, 302, 1716–1719, 2003.
- Arnold, F: Atmospheric aerosol and cloud condensation nuclei formation: A possible influence of cosmic rays?, *Space Sci. Rev.*, 125, 169–186, 2006.
- 5 Bae, M.-S., Schauer, J. J., DeMinter, J. T., Turner, J. R., Smith D., and Cary, R. A.: Validation of a semi-continuous instrument for elemental carbon and organic carbon using a thermal-optical method, *Atmos. Environ.*, 38, 2885–2893, 2004.
- Buzorius, G., McNaughton, C. S., Clarke, A. D., Covert, D. S., Blomquist, B., Nielsen, K., and Brechtel, F. J.: Secondary aerosol formation in continental outflow conditions during ACE-10 Asia, *J. Geophys. Res.*, 109, D24203, doi:10.1029/2004JD004749, 2004.
- Cantrell, W., Shaw, G., Cass, G. R., Chowdhury, Z., Hughes, L. S., Prather, K. A., Guazzotti, S. A., and Coffee, K. R.: Closure between aerosol particles and cloud condensation nuclei at Kaashidhoo Climate Observatory, *J. Geophys. Res.*, 106(D22), 28 711–28 718, 2001.
- 15 Carmichael, G. R., Hong, M., Ueda, H., Chen, L., Murano, K., Park, J. K., Lee, H., Kim, Y., Kang, C., and Shim, S.: Aerosol composition at Cheju Island, Korea, *J. Geophys. Res.*, 102(D5), 6047–6062, 1997.
- Cavalli, F., Facchini, M. C., Decesari, S., et al.: Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic, *J. Geophys. Res.*, 109, D24215, doi:10.1029/2004JD005137, 2004.
- 20 Chameides, W. L., Luo, C., Saylor, R., Streets, D. G., Huang, Y., Bergin, M., and Giorgi, F.: Correlation between model-calculated anthropogenic aerosols and satellite-derived cloud optical depths: Indication of indirect effect?, *J. Geophys. Res.*, 107(D10), 4085, doi:10.1029/2000JD000208, 2002.
- Clegg, S. L., Rard, J. A., and Pitzer, K. S.: Thermodynamic properties of 0-6 mol Kg<sup>-1</sup> aqueous sulfuric acid from 273.15 K to 328.15 K, *J. Chem. Soc. Faraday Trans.*, 90, 1875–1894, 1994.
- 25 Clegg, S. L., Milioto, S., and Palmer, D. A.: Osmotic and activity coefficients of aqueous (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as a function of temperature, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> – H<sub>2</sub>SO<sub>4</sub> mixtures at 298.15 K and 323.15 K, *J. Chem. Eng. Data*, 41, 455–467, 1996.
- Corrigan, C. E. and Novakov, T.: Cloud condensation nucleus activity of organic compounds: A laboratory study, *Atmos. Environ.*, 33, 2661–2668, 1999.
- 30 Covert, D. S., Gras, J. L., Wiedensohler A., and Stratmann F.: Comparison of directly measured CCN with CCN modeled from the number-size distribution in the marine boundary layer

ACPD

7, 15805–15851, 2007

## CCN activity at Jeju Island, 2005

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

- during ACE 1 at Cape Grim, Tasmania, *J. Geophys. Res.*, 103(D13), 16 597–16 608, 1998.
- Decesari, S., Facchini, M. C., Fuzzi, S., McFiggans, G. B., Coe, H., and Bower, K. N.: The water-soluble organic component of size-segregated aerosol, cloud water and wet depositions from Jeju Island during ACE-Asia, *Atmos. Environ.*, 39, 211–222, 2005.
- 5 Dinar, E., Taraniuk, I., Graber, E. R., Katsman, S., Moise, T., Anttila, T., Mentel, T. F., and Rudich, Y.: Cloud Condensation Nuclei properties of model and atmospheric HULIS, *Atmos. Chem. Phys.*, 6, 2465–2481, 2006a.
- Dinar, E., Mentel, T. F., and Rudich, Y.: The density of humic acids and humic like substances (HULIS) from fresh and aged wood burning and pollution aerosol particles, *Atmos. Chem. Phys.*, 6, 5213–5224, 2006b.
- 10 Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F., Hings, S., Jung, D., Borrmann, S., and Andreae, M. O.: Size matters more than chemistry for cloud-nucleating ability of aerosol particles, *Science*, 312, 1375–1378, 2006.
- 15 Facchini, M. C., Mircea, M., Fuzzi, S., and Charlson, R. J.: Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, 401, 257–259, 1999.
- Grabber, E. R. and Rudich, Y.: Atmospheric HULIS: How humic-like are they? A comprehensive and critical review, *Atmos. Phys. Chem.*, 6, 729–753, 2006.
- Hoffer, A., Gelencsèr, A., Guyon, P., Kiss, G., Schmid, O., Frank, G. P., Artaxo, P., and Andrea, M. O.: Optical properties of humic-like substances (HULIS) in biomass-burning aerosols, *Atmos. Chem. Phys.*, 6, 3563–3570, 2006,  
<http://www.atmos-chem-phys.net/6/3563/2006/>.
- 20 Hudson, J. G. and Yum, S. S.: Cloud condensation nuclei spectra and polluted and clean clouds over the Indian Ocean, *J. Geophys. Res.*, 107(D19), 8022, doi:10.1029/2001JD000829, 2002.
- 25 Kawamoto, K., Hayasaka, T., Uno, I., and Ohara, T.: A correlative study on the relationship between modeled anthropogenic aerosol concentration and satellite-observed cloud properties over east Asia, *J. Geophys. Res.*, 111, D19201, doi:10.1029/2005JD006919, 2006.
- Kawamura, K., Umemoto, N., Mochida, M., Bertram, T., Howell, S., and Huebert, B. J.: Water-soluble dicarboxylic acids in the tropospheric aerosols collected over east Asia and western North Pacific by ACE-Asia C-130 aircraft, *J. Geophys. Res.*, 108(D23), 8639, doi:10.1029/2002JD003256, 2003.
- 30 Kim, J., Yoon, S.-C., Jefferson, A., Kim, S.-W.: Aerosol hygroscopic properties during Asian dust

---

**CCN activity at Jeju Island, 2005**M. Kuwata et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- pollution, and biomass burning episodes at Gosan, Korea in April 2001, *Atmos. Environ.*, 40, 1550–1560, 2006.
- Kiss, G, Tombàcz, E., and Hanson, H.-C.: Surface tension effects of Humic-like substances in the aqueous extract of tropospheric fine aerosol, *J. Atmos. Chem.*, 50, 279–294, 2005.
- 5 Knutson, E. O. and Whitby, K. T.: Aerosol classification by electric mobility: Apparatus, theory, and applications, *J. Aerosol. Sci.*, 6, 443–451, 1975.
- Kondo, Y., Komazaki, Y., Miyazaki, Y., et al.: Temporal variations of elemental carbon in Tokyo, *J. Geophys. Res.*, 111, D12205, doi:10.1029/2005JD006257, 2006.
- 10 Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R. J., Jimenez, J. L., Zhang, Q., and Worsnop, D. R.: Oxygenated and water-soluble organic aerosols in Tokyo, *J. Geophys. Res.*, 112, D01203, doi:10.1029/2006JD007056, 2007.
- Kreidenweis, S. M., Koehler, K., DeMott, P. J., Prenni, A. J., Carrico, C., and Ervens, B.: Water activity and activation diameters from hygroscopicity data – Part I: Theory and application to inorganic salts, *Atmos. Chem. Phys.*, 5, 1357–1370, 2005
- 15 Kuwata, M., Kondo, Y., Mochida, M., Takegawa, N., and Kawamura, K.: Dependence of CCN activity of less volatile particles on the amount of coating observed in Tokyo, *J. Geophys. Res.*, 112, D11207, doi:10.1029/2006JD007758, 2007.
- Laaksonen, A., Hamed, A., Joutsensaari, J., Hiltunen, L., Cavalli, F., Junkermann, W., Asmi, A., Fuzzi, S., and Facchini, M. C.: Cloud condensation nucleus production from nucleation events at a highly polluted region, *Geophys. Res. Lett.*, 32, L06812, doi:10.1029/2004GL022092, 2005.
- 20 Lee, J. Y., Kim, Y. P., Kang, C.-H., Ghim, Y. S., and Kaneyasu, N.: Temporal trend and long-range transport of particulate polycyclic aromatic hydrocarbons at Gosan in northeast Asia between 2001 and 2004, *J. Geophys. Res.*, 111, D11303, doi:10.1029/2005JD006537, 2006.
- 25 Lohmann, U. and Feichter, J.: Global indirect aerosol effects: a review, *Atmos. Chem. Phys.*, 5, 715–737, 2005,  
<http://www.atmos-chem-phys.net/5/715/2005/>.
- Markowski, G. R.: Improving Twomey's algorithm for inversion of aerosol measurement data, *Aerosol. Sci. Technol.*, 7, 127–141, 1987.
- 30 McFiggans, G., Artaxo, P., Baltensperger, U., et al.: The effect of physical and chemical aerosol properties on warm cloud droplet activation, *Atmos. Chem. Phys.*, 6, 2593–2649, 2006,  
<http://www.atmos-chem-phys.net/6/2593/2006/>.

---

**CCN activity at Jeju Island, 2005**M. Kuwata et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Matsumoto, K., H. Tanaka, H., Nagao, I., and Ishizaka, Y.: Contribution of particulate sulfate and organic carbon to cloud condensation nuclei in the marine atmosphere, *Geophys. Res. Lett.*, 24(6), 655–658, 1997.
- Medina, J., Nenes, A., Sotiropoulou, R.-E. P., Cottrell, L. D., Ziemba, L. D., Beckman, P. J., and Griffin, R. J.: Cloud condensation nuclei closure during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign: Effects of size-resolved composition, *J. Geophys. Res.*, 112, D10S31, doi:10.1029/2006JD007588, 2007.
- Miyazaki, Y., Kondo, Y., Takegawa, N., Komazaki, Y., Fukuda, M., Kawamura, K., Mochida, M., Okuzawa, K., and Weber, R. J.: Time-resolved measurements of water-soluble organic carbon in Tokyo, *J. Geophys. Res.*, 111, D23206, doi:10.1029/2006JD007125, 2006.
- Miyazaki, Y., Kondo, Y., Kodama, D., Han, S., Koike, M., Komazaki, Y., Tanimoto, H., and Matsueda, H.: Chemical characteristics of water-soluble organic carbon in the Asian outflow, *J. Geophys. Res.*, in press, 2007.
- Mochida, M., Kawamura, K., Umemoto, N., Kobayashi, M., Matsunaga, S., Lim, H., Turpin, B. J., Bates, T. S., and Simoneit, B. R. T.: Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign, *J. Geophys. Res.*, 108(D23), 8638, doi:10.1029/2002JD003249, 2003.
- Mochida, M., Kuwata, M., Miyakawa, T., Takegawa, N., Kawamura, K., and Kondo, Y.: Relationship between hygroscopicity and cloud condensation nuclei activity for urban aerosols in Tokyo, *J. Geophys. Res.*, 111, D23204, doi:10.1029/2005JD006980, 2006.
- Mochida, M., Umemoto, N., Kawamura, K., Lim, H.-J., and Turpin, B. J.: Bimodal size distributions of various organic acids and fatty acids in the marine atmosphere: Influence of anthropogenic aerosols, Asian dusts, and sea spray off the coast of East Asia, *J. Geophys. Res.*, 112, D15209, doi:10.1029/2006JD007773, 2007.
- O'Dowd, C. D., Hameri, K., Makela, J. M., et al.: A dedicated study of New Particle Formation and Fate in the Coastal Environment (PARFORCE): Overview of objectives and achievements, *J. Geophys. Res.*, 107(D19), 8108, doi:10.1029/2001JD000555, 2002.
- Orsini, D. A., Ma, Y., Sullivan, A., Sierau, B., Baumann, K., and Weber, R. J.: Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol composition, *Atmos. Environ.*, 37, 1243–1259, 2003.
- Pang Y., Turpin, B. J., and Gundel, L. A.: On the importance of organic oxygen for understanding organic aerosol particles, *Aerosol. Sci. Technol.*, 40, 128–133, 2006.

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Raymond, T. M. and Pandis, S. N.: Cloud activation of single-component organic aerosol particles, *J. Geophys. Res.*, 107(D24), 4787, doi:10.1029/2002JD002159, 2002.
- Reade, L., Jennings, S. G., and McSweeney, G.: Cloud condensation nuclei measurements at Mace Head, Ireland, over the period 1994–2002, *Atmos. Res.*, 82, 610–621, 2006.
- 5 Richter, A., Burrows, J. P., Nüb, C., Grainer, C., and Niemeier, U.: Increase in tropospheric nitrogen dioxide over China observed from space, *Nature*, 437, 129–132, 2005.
- Roberts, G. C., Artaxo, P., Zhou, J., Swietlicki, E., and Andreae, M. O.: Sensitivity of CCN spectra on chemical and physical properties of aerosol: A case study from the Amazon Basin, *J. Geophys. Res.*, 107(D20), 8070, doi:10.1029/2001JD000583, 2002.
- 10 Roberts, G. C., and Nenes, A.: A continuous-flow streamwise thermal gradient CCN chamber for atmospheric measurements, *Aerosol Sci. Tech.*, 39, 206–221, 2005.
- Sawa, Y., Tanimoto, H., Yonemura, S., Matsueda, H., Wada, A., Taguchi, S., Hayasaka, T., Tsuruta, H., Tohjima, Y., and Mukai, H.: Widespread pollution events of carbon monoxide observed over the western North Pacific during the EAREX 2005 campaign, *J. Geophys. Res.*, 112, D22S26, doi:10.1029/2006JD008055, 2007.
- 15 Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics*, John Wiley & Sons, Inc, New York, 2006.
- Simoneit, B. R. T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H.-J., Turpin, B. J., and Komazaki, Y.: Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign, *J. Geophys. Res.*, 109, D19S10, doi:10.1029/2004JD004598, 2004.
- 20 Sotiropoulou, R. E. P., Tagaris, E., Pilinis, C., Anttila, T., and Kulmala, M.: Modeling new particle formation during air pollution episodes: Impacts on aerosol and cloud condensation nuclei, *Aerosol Sci. Tech.*, 40, 557–572, 2006.
- Streets, D. G., Tsai, N. Y., Akimoto, H., and Oka, K.: Sulfur dioxide emissions in Asia in the period 1985–1997, *Atmos. Environ.*, 34, 4413–4424, 2000.
- 25 Sullivan, A. P., Weber, R. J., Clements, A. L., Turner, J. R., Bae, M. S., and Schauer, J. J.: A method for on-line measurement of water-soluble organic carbon in ambient aerosol particles: Results from an urban site, *Geophys. Res. Lett.*, 31, L13105, doi:10.1029/2004GL019681, 2004.
- 30 Takegawa, N., Miyazaki, Y., Kondo, Y., Komazaki, Y., T. Miyakawa, T., Jimenez, J. L., Jayne, J. T., Worsnop, D. R., Allan, J., and Weber, R. J.: Characterization of an Aerodyne Aerosol Mass Spectrometer (AMS): Intercomparison with other aerosol instruments, *Aerosol Sci.*

Tech., 39, 760–770, 2005.

Topping, D., Coe, H., McFiggans, Burgess, G. R., Allan, J., Alfarra, M. R., Bower, K., Choulaton, T. W., Decesari, S., and Facchini, M. C.: Aerosol chemical characteristics from sampling conducted on the Island of Jeju Korea during ACE Asia, *Atmos. Environ.*, 38, 2111–2123, 2004.

Twomey, S.: Pollution and the planetary albedo, *Atmos. Environ.*, 8, 1251–1256, 1974.

Van Reken, T. M., Rissman, T. A., Roberts, G. C., Varutbangkul, V., Jonsson, H. H., Flagan, R. C, and Seinfeld, J. H.: Toward aerosol/cloud condensation nuclei (CCN) closure during CRYSTAL-FACE, *J. Geophys. Res.*, 108(D20), 4633, doi:10.1029/2003JD003582, 2003.

Yum, S. S., Hudson, J. G., Song, K. Y., and Choi, B.-C.: Springtime cloud condensation nuclei concentrations on the west coast of Korea, *Geophys. Res. Lett.*, 32, L09814, doi:10.1029/2005GL022641, 2005.

Yum, S. S., Roberts, G., Kim, J. H., Song, K., and Kim, D.: Submicron aerosol size distributions and cloud condensation nuclei concentrations measured at Gosan, Korea during the ABC-EAREX 2005, *J. Geophys. Res.*, 112, D22S32, doi:10.1029/2006JD008212, 2007.

Wiedensohler, A.: Technical Note. An Approximation of the bipolar charge distribution for particles in the submicron size range, *J. Aerosol Sci.*, 19, 387–389, 1988.

ACPD

7, 15805–15851, 2007

---

## CCN activity at Jeju Island, 2005

M. Kuwata et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

## CCN activity at Jeju Island, 2005

M. Kuwata et al.

**Table 1.** Calibration results and operating conditions of the CCN measurement system shown in Fig. 1. *SS* was calculated at 300 K and 72 mN/m by the ideal solution approximation. The values in parentheses show *SS* calculated using the osmotic coefficient of Clegg et al. (1996).

$\Delta T$ (K)	Activation dry diameter of $(\text{NH}_4)_2\text{SO}_4$ (nm)	<i>SS</i> (%)	The particle diameters classified by the DMA (nm)
3.08	125±3	0.097 (0.10)	80, 100, 110, 120, 130, 140, 160, 180, 200, 240, 290
4.62	63±2	0.27 (0.30)	60, 65, 70, 75, 80, 85, 90, 100, 130, 160, 200, 240, 290
9.24	38±1	0.58 (0.65)	35, 40, 45, 50, 60, 70, 80, 100, 130, 160, 200, 240, 290
15.4	27±1	0.97 (1.1)	25, 30, 35, 40, 50, 60, 80, 100, 130, 160, 200, 240, 290

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[I◀](#)
[▶I](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

**Table 2.** Average values and standard deviations of the CCN number concentration,  $D_{50}$ , and  $B$ . The surface tension of water was assumed for the calculation of  $B$ .

SS (%)	CCN number concentration ( $\text{cm}^{-3}$ )	$D_{50}$ (nm)	$B$
0.097	1194±746	136±17	0.61±0.17
0.27	2543±1277	71±6	0.55±0.12
0.58	3496±1510	44±3	0.50±0.09
0.97	3996±1686	31±3	0.55±0.13

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**CCN activity at Jeju Island, 2005**

M. Kuwata et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)**Table 3.** Average concentration of inorganic components during the observation period.

$\text{NH}_4^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$
1.57 ( $\mu\text{g}/\text{m}^3$ )	0.38	0.26	0.43	0.18	1.44	3.96	0.49

## CCN activity at Jeju Island, 2005

M. Kuwata et al.

**Table 4.** Values used for the calculation of  $D_{\text{crit}}$ .  $\nu$  for WIOC and EC are not shown here because they are insoluble in water.

	Assumed composition	Molecular weight (MW)	$\nu$	$\rho$ (g/cm <sup>3</sup> )
Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132.14	3	1.77
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	80.04	2	1.72
WSOC (oxalic acid)	(COOH) <sub>2</sub>	90.04	1	1.9
WSOC (adipic acid)	HOOC(CH <sub>2</sub> ) <sub>4</sub> COOH	146.14	1	1.36
WSOC (HULIS)	CH <sub>1.16</sub> O <sub>0.63</sub>	700	1	1.5
WIOC	(-CH <sub>2</sub> -)	14/carbon atom	N/A	0.8
EC	C (graphite)	12/carbon atom	N/A	2.0

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[I◀](#)
[▶I](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)



## CCN activity at Jeju Island, 2005

M. Kuwata et al.

**Table 5.** Differences between  $D_{50}$  (observed) and calculated  $D_{\text{crit}}$  ( $D_{\text{crit}} - D_{50}$ ). The values in parentheses show the magnitude of the difference in %. “Oxalic acid”, “adipic acid”, and “HULIS” show that the oxalic acid, adipic acid and HULIS assumptions, respectively.

	SS =0.097%	0.27%	0.58%	0.97%
Oxalic acid	27±18 (nm) (20±12%)	13±10 (18±13%)	7±7 (16±15%)	6±6 (21±19%)
Adipic acid	34±19 (26±13%)	17±11 (24±15%)	9±8 (22±17%)	8±6 (27±22%)
HULIS	39±20 (29±14%)	17±12 (25±16%)	10±8 (23±18%)	8±7 (26±23%)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## CCN activity at Jeju Island, 2005

M. Kuwata et al.

**Table 6.**  $D_{\text{crit}}$  for each SS calculated using the chemical composition given by Mochida et al. (2007).

	SS=0.097%	0.27%	0.58%	0.97%
Mochida et al. (2007)	142 (nm)	72	43	31
$D_{50}$	136±17	71±6	44±3	31±3

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

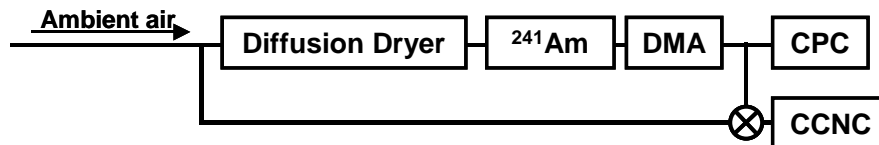
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**CCN activity at Jeju  
Island, 2005**

M. Kuwata et al.



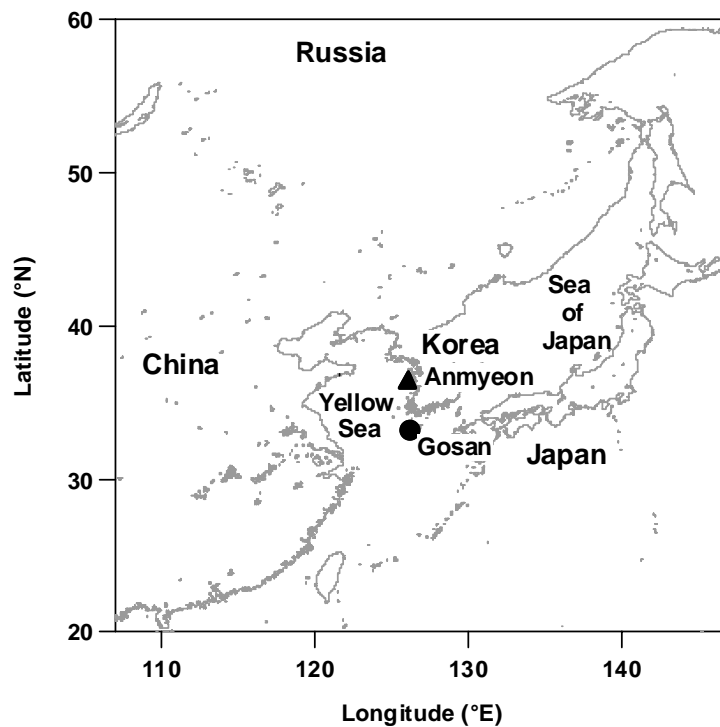
**Fig. 1.** CCN observation system used for this study. The three-way valve placed upstream of the CCN counter was used to select the sampling mode (see text for detailed explanation).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

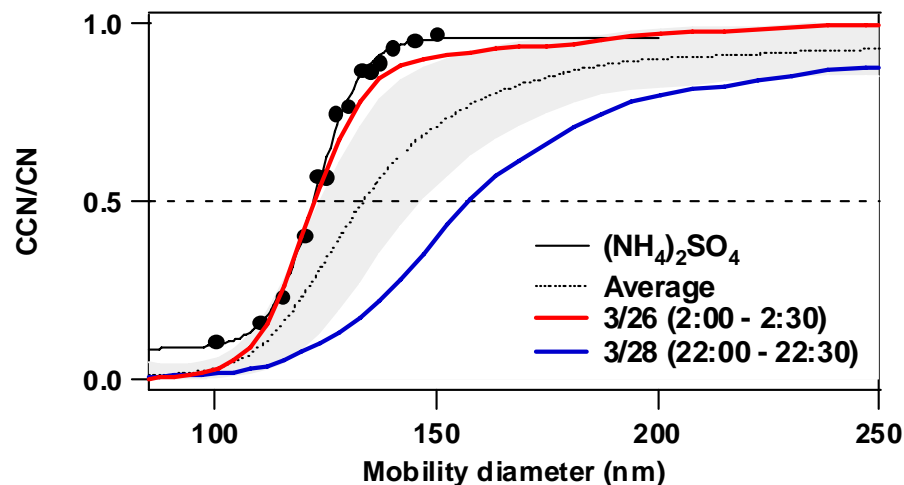
**CCN activity at Jeju  
Island, 2005**

M. Kuwata et al.

**Fig. 2.** Map of Gosan and surrounding region.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## CCN activity at Jeju Island, 2005

M. Kuwata et al.



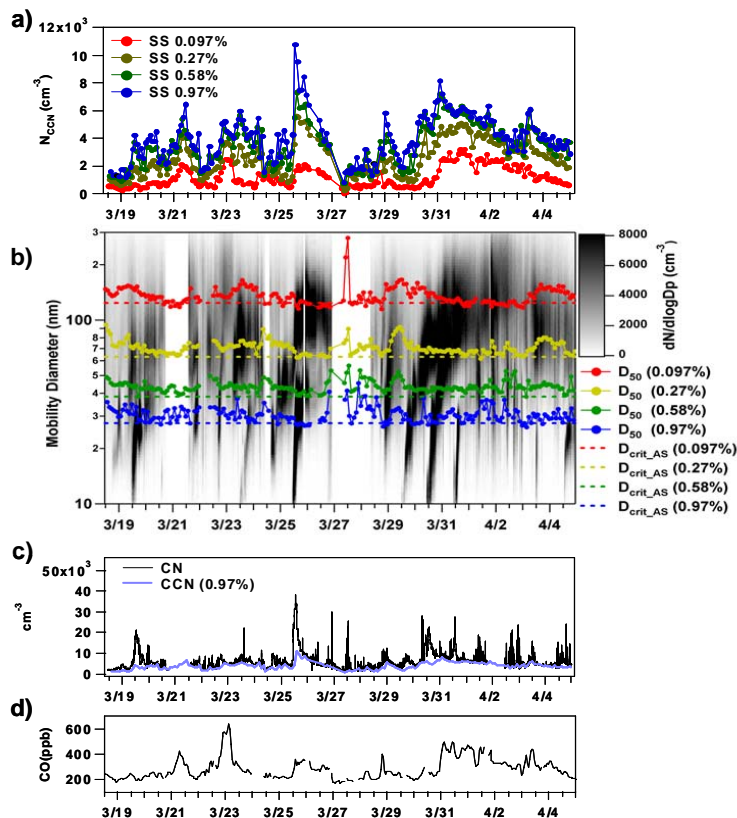
**Fig. 3.** Size distributions of CCN/CN ratios of ammonium sulfate and atmospheric particles at  $SS=0.097\%$ . The average, standard deviation, and two examples of CCN/CN during the observation period are shown. The solid circles denote the experimental data for ammonium sulfate under the observation conditions and the solid line shows the fitting results of the experimental data.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

CCN activity at Jeju  
Island, 2005

M. Kuwata et al.



**Fig. 4.** Time series of **(a)** CCN number concentration, **(b)** aerosol size distribution,  $D_{50}$ , **(c)** CN concentration, CCN (SS=0.97%) concentration, and **(d)** CO concentration. The dashed line in **(b)** shows the  $D_{crit}$  of ammonium sulfate at each SS.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

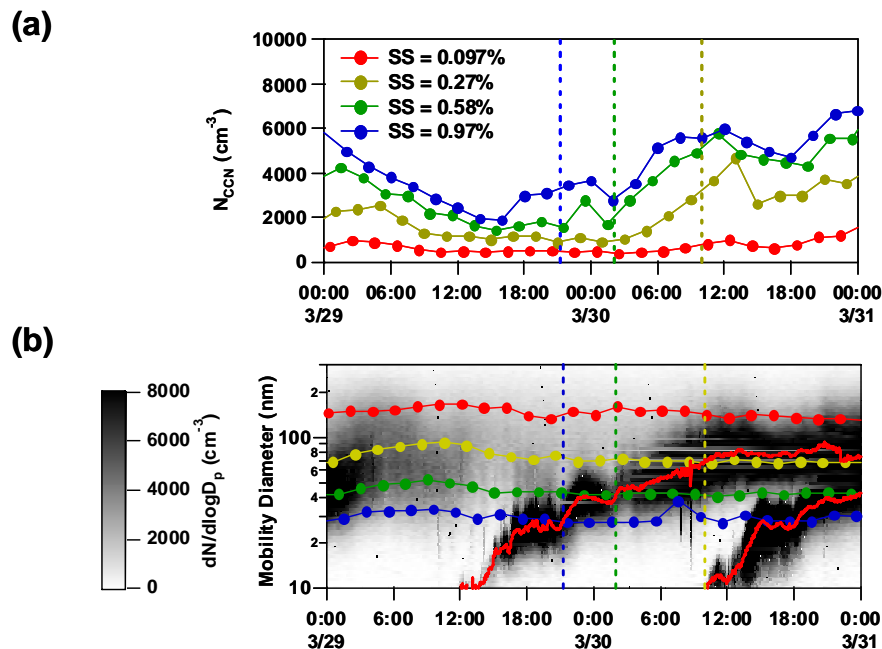
Printer-friendly Version

Interactive Discussion

EGU

## CCN activity at Jeju Island, 2005

M. Kuwata et al.



**Fig. 5.** Close-up of Fig. 4 during the new particle formation events from 29 March to 31 March. The (a) time series of CCN number concentration and (b) the number size distribution and  $D_{50}$  are shown. The red lines in (b) denote the peak diameters obtained by bimodal lognormal fitting. The vertical dashed lines show the time at which the peak diameter and  $D_{50}$  were equal.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

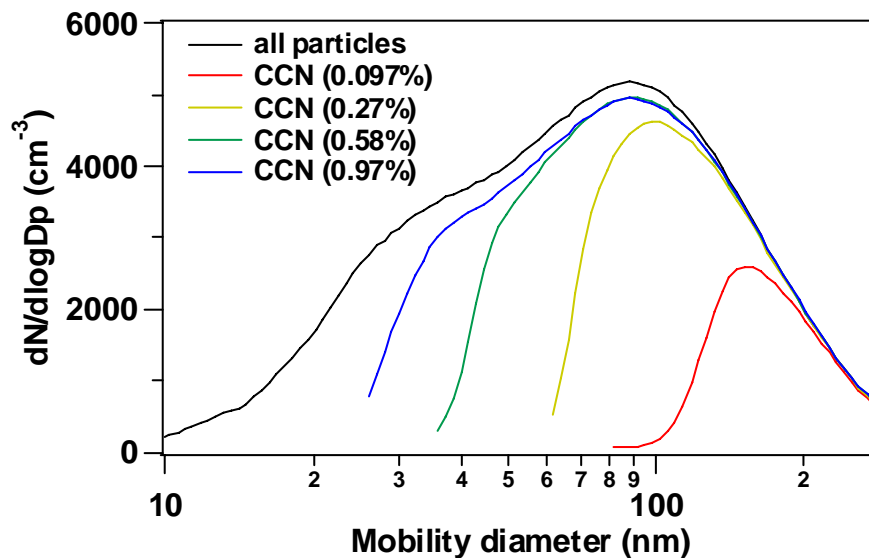
Printer-friendly Version

Interactive Discussion

EGU

## CCN activity at Jeju Island, 2005

M. Kuwata et al.



**Fig. 6.** Number size distribution of particles and CCN. CCN size distributions were estimated by multiplying CCN/CN ratios by the number size distribution. The data are averaged over the whole observation period. The data range of CCN size distributions are limited by the scanning range of the DMA.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU



CCN activity at Jeju  
Island, 2005

M. Kuwata et al.

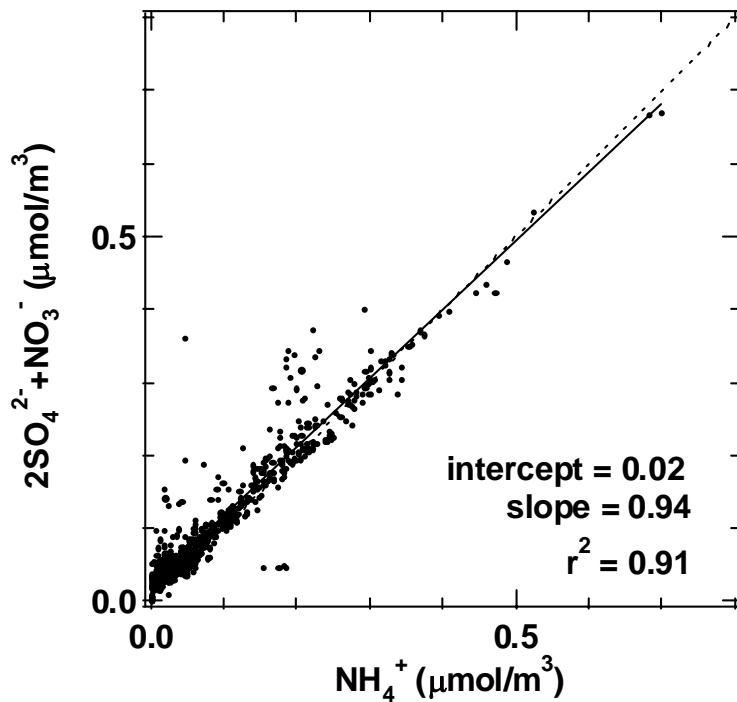


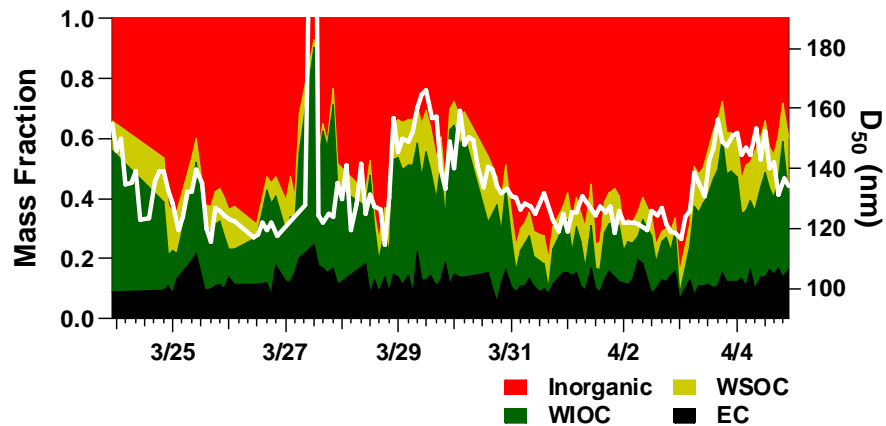
Fig. 7. Ion balance between ammonium, sulfate, and nitrate ions.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

CCN activity at Jeju  
Island, 2005

M. Kuwata et al.



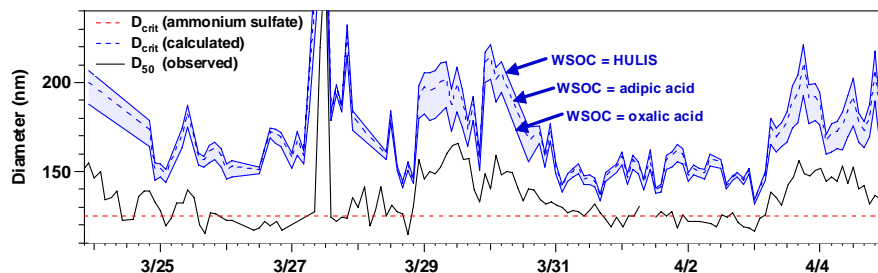
**Fig. 8.** Temporal variation of the mass fraction of aerosol components and  $D_{50}$  at  $SS=0.097\%$ . Here, “inorganic” denotes the summation of ammonium sulfate and ammonium nitrate.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

## CCN activity at Jeju Island, 2005

M. Kuwata et al.



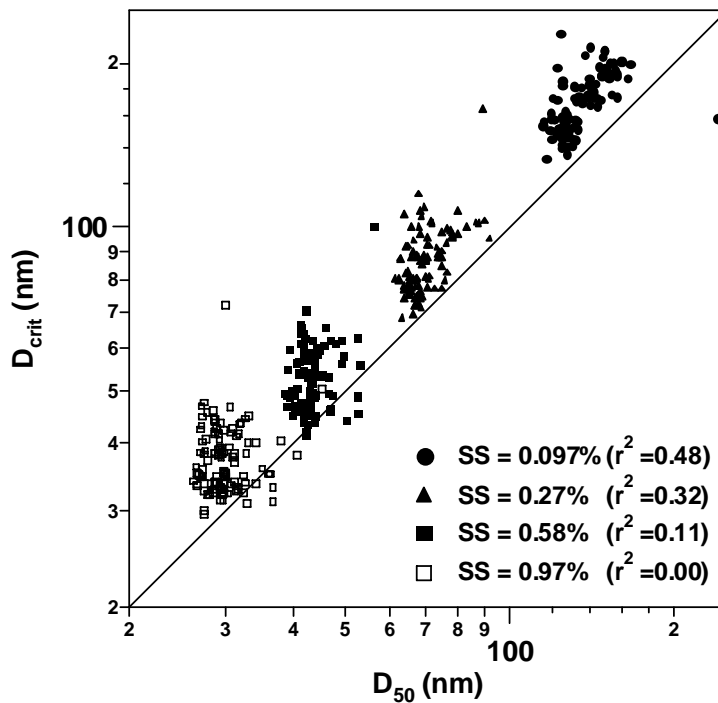
**Fig. 9.** Comparison of observed  $D_{50}$  and calculated  $D_{crit}$  at  $SS=0.097\%$ . The upper and lower blue lines were calculated using the “HULIS assumption” and “oxalic acid assumption,” respectively. See text for details of the calculations.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

CCN activity at Jeju  
Island, 2005

M. Kuwata et al.



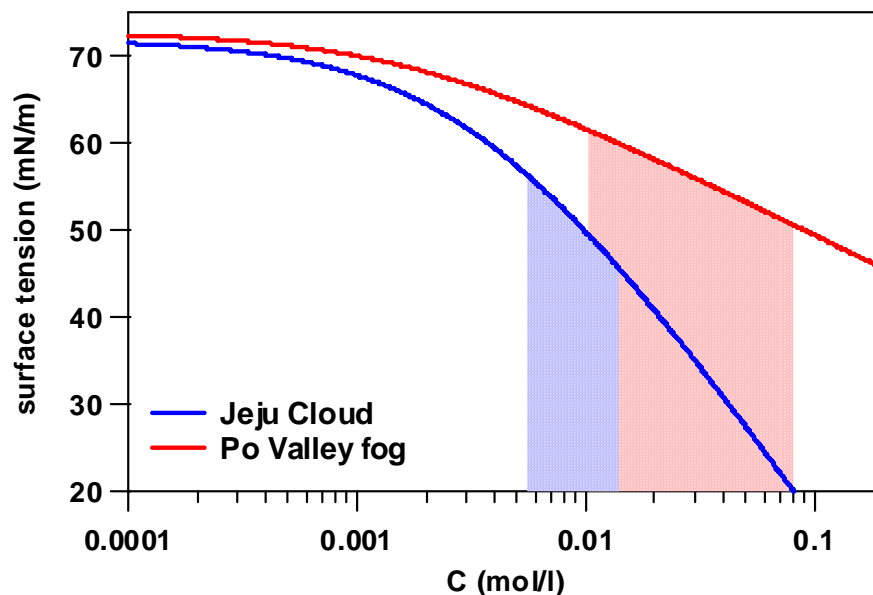
**Fig. 10.** Scatter plot of  $D_{50}$  (observed) and calculated  $D_{crit}$  (calculated). The adipic acid assumption was used for the calculation shown in this figure.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

CCN activity at Jeju  
Island, 2005

M. Kuwata et al.



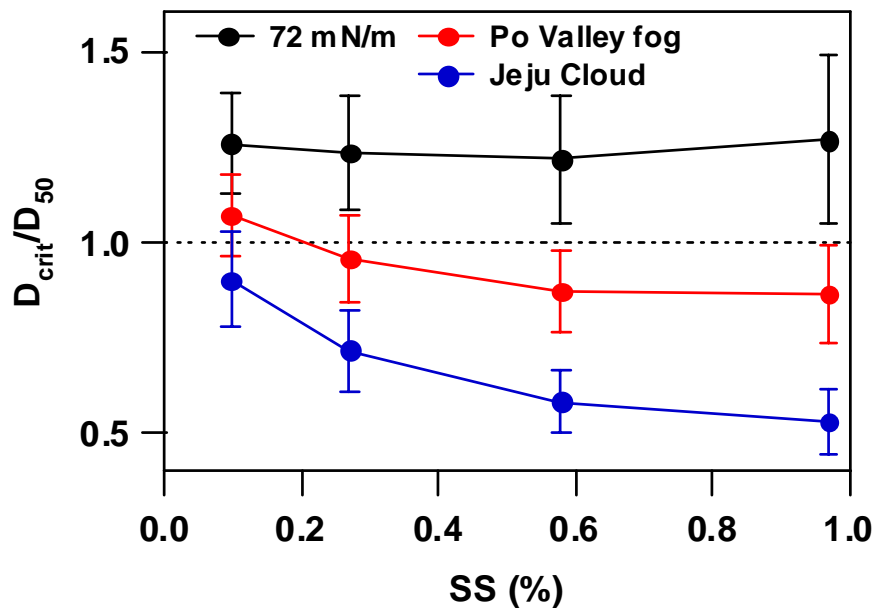
**Fig. 11.** Decrease of surface tension calculated using the parameters for Jeju cloud water and Po Valley fog by McFiggans et al. (2006). The colored area in the figure corresponds to the values at the critical SSs.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

CCN activity at Jeju  
Island, 2005

M. Kuwata et al.



**Fig. 12.** Comparison of  $D_{crit}/D_{50}$  calculated using several surface tension parameters. The calculation was performed using the adipic acid approximation.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU

CCN activity at Jeju  
Island, 2005

M. Kuwata et al.

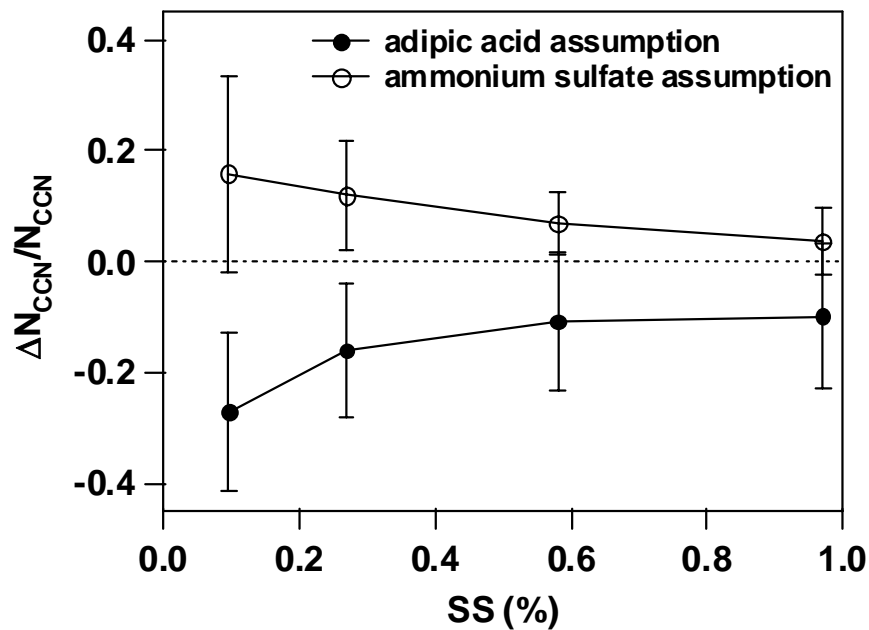


Fig. 13. Average values and standard deviations of  $\Delta N_{\text{CCN}}/N_{\text{CCN}}$ .

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EGU