

# Simultaneous Measurement of CCN Activity and Chemical Composition of Fine-Mode Aerosols at Noto Peninsula, Japan, in Autumn 2012

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# ABSTRACT

Size resolved CCN activity and bulk chemical composition of atmospheric aerosols in the submicrometer size range were measured at Noto Ground-based Research Observatory (NOTOGRO), facing the Sea of Japan at the tip of Noto Peninsula, in autumn 2012. In the atmospheric measurement, the CCN efficiency spectra, where the CCN number fraction is plotted against the diameter of aerosols, were obtained for four different supersaturation (SS) conditions. The hygroscopicity parameter  $\kappa$ , which depends on the chemical composition of aerosols, was estimated from analysis of the CCN spectra. The CCN activation diameters of ambient aerosols were clearly larger than those of pure ammonium sulfate under all SS conditions. The bulk chemical composition derived by an aerosol chemical speciation monitor (ACSM) also indicated the significant mass fraction of organics in the submicrometer size range. The relationship between the estimated  $\kappa$  values and the CCN activation diameters suggests that organics contribute the aerosol mass especially in the size range of less than 100 nm. The contribution of organics observed in this study was more apparent than those of other sites in East Asia. The mass concentrations and chemical compositions of the aerosols varied with trajectory pathway, which caused large fluctuations in  $\kappa$  values especially at higher SS conditions. The negative correlations (0.13% and 0.25%), suggesting that less-hygroscopic organics, that can suppress the initial growth rates of cloud droplets, were included during the periods of large organic mass concentrations.

*Keywords:* Hygroscopicity parameter; Cloud droplet growth; Organic aerosols; Aerosol chemical speciation monitor; East Asia.

# INTRODUCTION

Atmospheric aerosols play an important role in controlling the Earth's radiation balance and/or the hydrological system by acting as cloud condensation nuclei (CCN). Perturbation of CCN number concentrations may have a significant impact on the optical properties and/or lifetime of clouds. However, a large uncertainty in the understanding of the Earth's radiation balance stems from the complexity of such interaction between atmospheric aerosols and clouds (IPCC, 2013). To

Tel.: +81-76-264-6510; Fax: +81-76-264-6564 *E-mail address:* matsuki@staff.kanazawa-u.ac.jp assess the impact of the aerosol-cloud interaction on the Earth's climate and refine numerical model predictions of climate change, it is essential to know physical and chemical properties of ambient aerosols that act as CCN.

For quantitative evaluation of CCN activity of ambient aerosols, it is important to know the size and chemical composition of aerosols, as well as the water vapor supersaturation (hereafter referred to as SS) of the environment. Thus, simultaneous measurement of sizesegregated CCN activity and chemical composition of the ambient aerosols under controlled SS conditions is an effective method for better characterizing CCN activity of the ambient aerosols (e.g., Gunthe *et al.*, 2009; Mochida *et al.*, 2010; Rose *et al.*, 2010).

Some inorganic aerosols such as ammonium sulfate  $((NH_4)_2SO_4)$  are known as most effective and important CCN in the atmosphere (e.g., Pruppacher and Klett, 1997). Previous observational studies have reported that organic aerosols also contribute significantly to CCN number concentrations (Navakov and Penner, 1993; Matsumoto *et* 

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*al.*, 1998). Organics potentially play an important role in regulating the CCN activity of atmospheric aerosols (e.g., Hori *et al.*, 2003), and comprise a substantial fraction (around 20% to 90%) of the submicrometer aerosol mass (Jimenez *et al.*, 2009). Thus, it is important to know how the organics in the aerosols affect their CCN properties in the ambient atmosphere.

After aerosol particles are activated as cloud droplets under a certain SS condition, the particles grow larger by condensation of water molecules on the droplets. Generally, SS controls the growth rate of cloud droplets. Recent studies, however, reported that aerosol chemistry also affects the initial stage of droplet growth, and results in changes of cloud droplet number concentrations (e.g., Shantz *et al.*, 2010). For example, if the ambient aerosols include hydrophobic and/or glassy state organics, the growth rates of droplets might become suppressed (e.g., Cerruly *et al.*, 2011). The relationship between aerosol chemistry and droplet growth kinetics remains a controversial issue.

East Asia is the region where the highest CCN number concentration has been predicted (e.g., Spracklen et al., 2011). This is because the emission of anthropogenic pollutants from industrial regions caused by the continuous increase in economic activity. The pollutants are transported by the prevailing wind (mainly westward or northwest-ward) as the "Asian outflow", and may impact the regional climate. To investigate the characteristics of CCN properties or chemical compositions of fine-mode aerosols in the Asian outflow, several observations have been conducted in remote monitoring sites in East Asia such as Jeju Island, Korea (e.g., Topping et al., 2004; Kuwata and Kondo, 2008), Okinawa Island, Japan (e.g., Takami et al., 2007; Mochida et al., 2010) and Fukue Island, Japan (e.g., Takami et al., 2005). Indeed, these remote super-sites are well located for characterizing the Asian outflow directly downwind of central or south China where industrial activity is particularly concentrated (Fig. 1), but may not necessarily represent the entire regions along the western Pacific rim (may not always be suited for

monitoring the outflow e.g., from north China or Russia).

In this study, we performed simultaneous measurement of CCN activity and chemical composition of fine-mode aerosols (less than ca. 1 µm in diameter) at Noto Peninsula, Japan. This site was chosen since it is a remote site in central Japan which is more strongly influenced by the air-mass transported from the northeastern parts of East Asia (Fig. 1), where comprehensive CCN characterization has not yet taken place. The size-resolved CCN number fractions (CCN efficiency spectra), as well as bulk chemical composition for the fine-mode aerosols were obtained. Here, the CCN activity of the ambient aerosols is evaluated using the hygroscopicity parameter  $\kappa$  (Petters and Kreidenweis, 2007), which is estimated from the CCN activation diameter under controlled SS conditions. The relationship between the chemical composition of the CCN and the cloud droplet growth is also discussed.

# **METHODS**

### NOTO Ground-Based Research Observatory

The atmospheric observations were performed at NOTO Ground-based Research Observatory (NOTOGRO; 37.45°N, 137.36°E), which is located at the tip of Noto Peninsula (Fig. 1). The peninsula extends from the west coast of mainland Japan and extends approximately 150 km into the Sea of Japan. Kanazawa and Toyama are the nearest provincial cities, located about 115 km southwest and 85 km south of the observation site, respectively (Fig. 1). The geographical location of the peninsula is considered ideal for baseline atmospheric monitoring in East Asia, since it is surrounded by the sea and isolated from major pollution sources. The atmospheric observations were conducted from 3 to 29 Oct 2012. During this period, the air masses came mainly from the northwest across the Sea of Japan, allowing the study of long-range transport of aerosols from the northeast part of Asian Continent.



Fig. 1. Location of the NOTOGRO site. Locations of other atmospheric observation sites listed in Table 1 are also indicated on the left panel.

#### Instrumental Setup

A schematic of the instrumental setup is presented in Fig. 2. Ambient aerosols were sampled through a  $PM_{10}$  inlet (14.7 m above the ground level, 78 L min<sup>-1</sup> flow rate) via a stainless steel line (O.D. 5.65 cm) to an isokinetic flow splitter housed in a room on the top level of a three-story building. The sample flow was then guided into several aerosol-detecting instruments downstream of the flow splitter.

One of the sampling lines was connected to the scanning mobility CCN analysis (SMCA) system (Moore et al., 2010). In the SMCA line, aerosol particles were dried with two diffusion dryers filled with silica gel. The dried aerosols were charge-neutralized using a 241 Am neutralizer and introduced into a differential mobility analyzer (DMA, Model 3081L, TSI Inc.) for size classification. The monodisperse aerosol particles were transferred to a water-based condensation particle counter (WCPC, Model 3785, TSI Inc.) and a continuous flow thermal gradient CCN counter (CCNC, CCN-100, Droplet Measurement Technologies) to measure the number concentration of condensation nuclei (CN)  $(N_{\rm CN})$  and CCN  $(N_{\rm CCN})$ , respectively. The sizes of activated CCN (droplets) as a function of initial dry diameter were also measured by an optical particle counter installed in the CCNC. The voltage applied to the DMA was scanned using the TSI Aerosol Instrument Manager software for the Scanning Mobility Particle Sizer. In this study, the CCNC was operated under four different SS conditions (0.13%, 0.25%, 0.52% and 0.81%), and the SS conditions were changed every 30 minutes. The SS conditions in the CCN counter were determined by the calibration using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles were generated by atomization of the aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Alfa Aeser, 99.95%) and introduced to the SMCA system. For the calibration, a Köhler model similar to the Reference Köhler model described by Brechtel and Kreidenweis (2000) was applied.

Another line was connected to an aerosol chemical

speciation monitor (ACSM, Aerodyne Research Inc.) to obtain the bulk chemical composition of non-refractory submicrometer-sized aerosols (NR-PM<sub>1</sub>). Chemical species resolved by the instrument includes organics, sulfate, nitrate, ammonium and chloride. A PM<sub>2.5</sub> cyclone (cut off size of 2.5  $\mu$ m at a flow rate of 3 L min<sup>-1</sup>) was installed in the upstream of the ACSM inlet to remove coarse particles. The ionization efficiency of nitrate and the relative ionization efficiencies of ammonium and sulfate were determined by the standard calibration procedure (Ng *et al.*, 2011) using NH<sub>4</sub>NO<sub>3</sub> (99.5%, Strem Chemicals) and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (99.95% Alfa Aesar). Note that RIE of sulfate (0.7) for our instrument was determined by the routine calibration procedures introduced after the campaign.

A collection efficiency (CE) of 0.3 was applied for the ACSM data. The value of CE was determined by comparing the mass concentrations derived by the ACSM to those measured by an off-line analysis in a field campaign at the NOTOGRO site in summer 2013. The filter samples were collected using a 9-stage Andersen sampler (model AN-200, Tokyo Dylec corp.) with a flow rate of 28.3 L min<sup>-1</sup>. Sampling duration was 1 week per sample. The filters were extracted and water-soluble inorganic components were analyzed by ion chromatography (IC). Sulfate  $(SO_4^{2-})$  and ammonium  $(NH_4^+)$  concentrations were integrated for the smallest 3 stages (including backup filter) to obtain the PM<sub>1.1</sub> fraction. Fig. 3 shows scatter plots of ACSM (y-axis; CE = 1 is assumed) versus IC (x-axis) measurements. The slopes of the scatter plots are 0.29 and 0.35 for sulfate and ammonium, respectively. The CE = 0.3 was tuned so that the ACSM derived sulfate and ammonium match the filter based analysis.

#### **Data Processing**

The CCN efficiency spectra, where  $N_{\rm CCN}/N_{\rm CN}$  (hereafter referred to as  $dN_{\rm CCN}/dN_{\rm CN}$ ) is plotted against the diameter of aerosols, were obtained every 5 minutes. The  $dN_{\rm CCN}/dN_{\rm CN}$  values were calculated by subtraction of the contribution



Fig. 2. Schematic of the instrumentation used in this study.



**Fig. 3.** Intercomparison of ACSM-derived (a) sulfate and (b) ammonium (y-axis) and those derived by IC (x-axis) during the period of filter sampling in NOTOGRO.

of multiply-charged particles from both CCN and CN (http://nenes.eas.gatech.edu/SMCA/; Moore *et al.*, 2010), and fitted with a cumulative Gaussian distribution function (Rose *et al.*, 2008):

$$\frac{dN_{\rm CCN}}{dN_{\rm CN}} = a \left( 1 + erf\left(\frac{d_{\rm m} - d_{\rm act}}{b\sqrt{2}}\right) \right). \tag{1}$$

Here, *a* is a half of the maximum of the fitted curve and *b* is the standard deviation of the cumulative Gaussian distribution function. The CCN activation diameter  $(d_{act})$  of the measured particles at the instrument SS is defined as the dry mobility diameter  $(d_m)$  at which  $dN_{CCN}/dN_{CN}$  from Eq. (1) reached 50% of the maximum. In the current experimental setup, six CCN efficiency spectra can be obtained under each SS condition that lasts for 30 minutes. To eliminate the data obtained under unstable SS conditions, only the middle three spectra were chosen and the arithmetic mean values of the fitting parameter  $d_{act}$  (and values derived from  $d_{act}$ ) are used in the analyses.

CCN activation of aerosols was described in terms of the Köhler equation, where the activation depends on the Raoult effect (a decrease in water vapor pressure caused by the presence of solute) and the Kelvin effect (an increase in water vapor pressure caused by curvature at the air-liquid interface). The equation can be re-written in terms of the hygroscopicity parameter  $\kappa_{CCN}$  as (Petters and Kreidenweis, 2007):

$$S = \frac{d_{\rm drop}^3 - d_p^3}{d_{\rm drop}^3 - d_p^3 \left(1 - \kappa_{\rm CCN}\right)} \exp\left(\frac{4\sigma_{\rm drop}M_{\rm w}}{RT\rho_{\rm w}d_{\rm drop}}\right),\tag{2}$$

where *S* is the saturation ratio of water vapor,  $\sigma_{drop}$  is the droplet surface tension,  $M_w$  is the molecular weight of water,  $\rho_w$  is the density of pure water, *R* is the universal gas constant, *T* is the droplet temperature,  $d_{drop}$  is the droplet diameter, and  $d_p$  is the dry particle diameter. The  $\kappa_{CCN}$  for ambient aerosols and calibration aerosols ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) were determined for each SS condition, so that the maximum point (i.e., critical super saturation) of the Köhler curve (Eq. (2)) for particles having a dry mobility diameter of  $d_{act}$  equals the instrument SS. The surface tension of pure water was used for  $\sigma_{drop}$  and the temperature dependence of  $\sigma_{drop}$  and  $\rho_w$  was considered. We regard the temperature at the top of the column of the CCN counter as the droplet temperature.

In this study,  $\kappa_{ACSM}$  was also calculated using Eq. (3) and compared to  $\kappa_{CCN}$ . The  $\kappa$  value for multi-component aerosol particles is given by the simple mixing rule under the Zdanovskii-Stokes-Robinson assumption. In this study, ammonium nitrate was not included in the equation due to negligible contribution. If the amibient aerosol is a mixture of pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and organics,  $\kappa$  for the ambient aerosol ( $\kappa_{ACSM}$ ) can be written as:

$$\kappa_{\rm ACSM} = \varepsilon_{\rm org} \, \kappa_{\rm org} + (1 - \varepsilon_{\rm org}) \kappa_{\rm AS} \tag{3}$$

where  $\varepsilon_{\rm org}$  is the organic volume fraction, and  $\kappa_{\rm org}$  and  $\kappa_{\rm AS}$ are  $\kappa$  for organics and pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, respectively. In the calculation, values of 0.61 (Petters and Kreidenweis, 2007) and 0 to 0.2 (Jimenez *et al.*, 2009) were used for  $\kappa_{\rm AS}$  and  $\kappa_{\rm org}$ , respectively.  $\varepsilon_{\rm org}$  was calculated from ACSM derived organic mass fraction assuming that densities of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ( $\rho_{\rm AS}$ ) and organics ( $\rho_{\rm org}$ ) are 1.77 and 1.90, respectively. We assumed that the value of  $\rho_{\rm org}$  was as large as that for oxalic acid, because Zhang *et al.* (2007) reported that organic aerosols observed in remote sites in East Asia were mostly oxygenated.

The sizes of cloud droplets activated from ambient aerosols  $(D_{\text{ambient}})$  were compared to those activated from laboratorygenerated (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles  $(D_{\text{AS}})$ , which can be regarded as representative inorganic CCN.  $D_{\text{ambient}}$  and  $D_{\text{AS}}$  were calculated by averaging the size of activated droplets grown from aerosol particles having a dry diameter of 160 to 240 nm. Note that the particle concentrations in the CCN chamber were below 30 cm<sup>-3</sup> and 1100 cm<sup>-3</sup> during the observation and calibration period, respectively: thus, the effect of water vapor depletion on droplet growth was negligible even under the lowest SS condition (0.13%) (Lathem and Nenes, 2011).

### **Backward Airmass Trajectories**

Five-days backward trajectories (start time: 0900 LT and 2100 LT of each day, where LT is local time) at the height of 500 m above the sea level were calculated to investigate the air mass origins. These were obtained by using the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT4) model (http://ready.arl.noaa.gov/H YSPLIT.php; Draxler *et al.*, 2012 and references there in).

#### **RESULTS AND DISCUSSION**

### Averaged CCN Efficiency Spectra and Related Parameters

The CCN spectra of ambient aerosols averaged over the entire observation period are shown in Fig. 4 for each of the different SS conditions. The spectra for pure  $(NH_4)_2SO_4$ obtained during the calibration are also shown for comparison. As seen in Fig. 4. the CCN activation diameters of ambient aerosols were clearly larger than those of pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosols under all SS conditions. Each CCN spectra was fitted using Eq. (1) to obtain  $d_{act}$ . The mean  $d_{act}$ (mean ± standard deviation) of ambisent aerosols were  $133.4 \pm 12.3$ ,  $93.2 \pm 11.3$ ,  $60.3 \pm 8.2$  and  $45.8 \pm 6.1$  nm under the 0.13%, 0.25%, 0.52% and 0.81% SS condition, respectively. The slope of the CCN efficiency spectra of ambient aerosols around the  $d_{act}$  were not as steep as those of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosols. These results suggest that ambient aerosols observed at NOTOGRO were less CCN-active than pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and had heterogeneous chemical composition in the size range around  $d_{act}$ . The  $dN_{CCN}/dN_{CN}$ approached 1 along with increased  $d_{\rm m}$ , indicating minor external mixing of hydrophobic particles, such as fresh soot particles (Kuwata and Kondo, 2008), during the observation period.

The mean  $\kappa_{\rm CCN}$  values (mean  $\pm$  standard deviation) of ambient aerosols observed at the NOTOGRO site were  $0.34 \pm 0.12$ ,  $0.28 \pm 0.09$ ,  $0.24 \pm 0.09$  and  $0.23 \pm 0.08$ , under the SS conditions of 0.12%, 0.25%, 0.52% and 0.81%, respectively. The  $\kappa_{CCN}$  obtained in this study falls in the range of continental  $\kappa$  (0.27 ± 0.21) calculated by a numerical model (Pringle et al., 2010). However, the  $\kappa_{\rm CCN}$  values were clearly smaller than those of previous studies in East Asia. The previously reported values such as  $0.49 \pm 0.09$ for Jeju Island, Korea (Kuwata et al., 2008) and 0.50  $\pm$ 0.05 for Okinawa Island, Japan (Mochida et al., 2010) were closer to the value of  $\kappa$  of pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (0.61; Petters and Kreidenweis, 2007). Note that  $\kappa_{CCN}$  values at other sites were calculated by the same method as used in this study, using the CCN activation diameter reported in the literature (Kuwata et al., 2008; Mochida et al., 2010). This result suggests that the contribution of organics was more apparent at the NOTOGRO site during autumn than those for other sites in East Asia.

The difference in  $\kappa_{CCN}$  values among the observation sites might be caused by differences in air mass origin. Most of  $(NH_4)_2SO_4$  in aerosol is derived from fossil fuel combustion, and high concentrations of  $(NH_4)_2SO_4$  have been observed under the influence of polluted continental air masses (e.g., Matsumoto *et al.*, 2003). As will be shown



(a) SS 0.13%

1.0

**Fig. 4.** Averaged CCN spectra of ambient aerosol (bold solid lines and open circles) and  $(NH_4)_2SO_4$  (thin solid lines) under SS conditions of (a) 0.13%, (b) 0.25%, (c) 0.52% and (d) 0.81%. Gray shades (for ambient aerosols) and black bars (for  $(NH_4)_2SO_4$  particles) indicate standard deviations of the  $N_{CCN}/N_{CN}$  ratio at each dry mobility diameter.

later, air masses reaching the NOTOGRO site mainly passed through North Korea, the northeastern part of China, Mongolia and Russia during the observation period. These areas are less affected by anthropogenic pollution than central east China, which may explain the smaller contribution of  $(NH_4)_2SO_4$  to fine-mode aerosol observed in the NOTOGRO site. A detailed discussion about the relationship between air mass origin and chemical compositions of aerosols is given in the following section.

Fig. 5 presents the relationship between  $d_{act}$  and  $\kappa_{CCN}$  values. The average size distribution during the observation period is also shown in Fig. 5. If the ambient aerosols are well-mixed and the chemical composition of aerosols is uniform, the  $\kappa_{CCN}$  values should be constant with aerosol diameter. However, the  $\kappa_{CCN}$  values tended to decrease with decreasing diameter, indicating that the ambient aerosols have a size-dependent chemical composition, and organics



**Fig. 5.** Relationship between CCN activation diameter ( $d_{act}$ ; mobility diameter based) and hygroscopicity parameter  $\kappa_{CCN}$ .  $\kappa$  values of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (pink dotted line) and organics (green shades) from the literature are also shown in the panel. The averaged number size distribution of the ambient aerosols is shown as a bold solid line.

contributed to the aerosol mass especially in the size range of less than 100 nm. This result is consistent with the shape of the CCN spectra (Fig. 4), i.e., the slopes of the CCN spectra under each SS condition are not as steep as the case with pure  $(NH_4)_2SO_4$ . A similar trend was observed in the aerosols collected in the Amazon forest (Gunthe *et al.*, 2009) and in the downwind region of a mega-city in China (Rose *et al.*, 2010).

#### Chemical Characteristics of NR-PM<sub>1</sub>

The temporal variations of mass concentration and mass fraction of NR-PM<sub>1</sub> are presented in Figs. 6(a) and 6(b), respectively. The mean mass concentration (mean  $\pm$  standard deviation) of organics, sulfate, ammonium and nitrate were  $2.7 \pm 1.8$ ,  $1.9 \pm 1.2$ ,  $0.6 \pm 0.5$ , and  $0.2 \pm 0.2 \ \mu g \ m^{-3}$  (Table 1). The low nitrate concentration indicates that the influence of local pollution (e.g., vehicular and/or ship exhaust) was small during the observation period. The mean value of the total mass concentration ( $5.4 \pm 3.2 \ \mu g \ m^{-3}$ ) was about half to two-thirds of those for other rural or remote sites in East Asia during spring, and almost the same level as the annual average mass concentration observed at Okinawa Island (Table 1). The average mass concentrations of NR-PM<sub>1</sub> observed at several urban sites in East Asia are also listed in Table 1 for reference.

Organics, sulfate and ammonium are three major components observed throughout the observation period and they account for more than 95% of total mass concentration (Fig. 6(b)). The mean organic mass fraction of 0.49 was larger than that of Jeju Island (0.41; Topping *et al.*, 2004), Okinawa Island (0.17 to 0.20; Takami *et al.*, 2007; Miyoshi *et al.*, 2013). This result is consistent with the smaller  $\kappa$  values as compared to those of Jeju Island (Kuwata *et al.*, 2008) and Okinawa Island (Mochida *et al.*, 2010). The mean organic mass fraction was comparable with that for Fukue Island (0.45; Takami *et al.*, 2005). The temporal variations

of organic mass fraction negatively correlated with  $\kappa_{CCN}$ under each SS condition (reflecting aerosol chemical composition around the corresponding activation diameter) (Fig. 6(c)). In other words, low  $\kappa_{CCN}$  values appeared when organic mass fractions were high. Note that there were missing CCNC data due to instrument failure for the time periods from 1100 LT 11 Oct to 0400 LT 12 Oct, from 2000 LT 15 Oct to 1100 LT 17 Oct, from 0500 LT 20 Oct to 2300 LT 21 Oct, and from 05:00 LT Oct 25 to 09:00 LT Oct 26.

The averaged fractions of m/z 44 in the organic mass spectrum (hereafter referred to as  $f_{44}$ ), an indicator of oxygenated organic aerosols, were  $0.20 \pm 0.07$ . This value was higher than those at Fukue Island (0.06 to 0.15; Takami *et al.*, 2005) and Okinawa Island (0.11 to 0.16; Takami *et al.*, 2007), indicating that organic aerosols observed at the NOTOGRO site were highly oxygenated (or aged). Furthermore,  $f_{44}$  observed in this study were comparable to the high end of  $f_{44}$  of oxygenated organic aerosols observed at Northern Hemisphere observation sites (Ng *et al.*, 2010).

By use of the organic mass fractions derived by ACSM  $(\varepsilon_{\text{org}})$  and Eq. (3), values of  $\kappa_{\text{ACSM}}$  were calculated. The mean values of  $\kappa_{ACSM}$  were estimated to be 0.3 to 0.4, which was in agreement with  $\kappa_{\rm CCN}$  under the lowest SS condition (0.13%). The temporal variation of  $\kappa_{ACSM}$  is also shown in Fig. 6(c). If we assume a lower density of organics ( $\rho_{org} <$ 1.9 g cm<sup>-3</sup>) instead, the  $\kappa_{ACSM}$  would be overestimated. This result also suggests that organic aerosols observed at the NOTOGRO site were highly oxygenated, and is consistent with the high  $f_{44}$  values. In the cases of higher SS conditions (0.25%–0.81%), the value of  $\kappa_{ACSM}$  with  $\rho_{org}$ of 1.9 g cm<sup>-3</sup> would still overestimate the  $\kappa_{\rm CCN}$ . This indicates a larger contribution of organics especially in the smaller size range of < 100 nm that is not resolved by the ACSM derived bulk chemistry, and supports the size-dependent chemical composition of the ambient aerosols (Fig. 5).



**Fig. 6.** Temporal variation of (a) mass concentrations of NR-PM<sub>1</sub>, (b) % mass fraction of each component, (c) hygroscopicity  $\kappa$  ( $\kappa_{CCN}$  and  $\kappa_{ACSM}$ ), (d) the diameters of droplets activated from the ambient ( $D_{ambient}$ ; open circles) and ammonium sulfate ( $D_{AS}$ ; solid lines) aerosols and (e)  $D_{ambient}/D_{AS}$ . Classifications of backward trajectories are also indicated at the top of the panel. Note that the range of  $\kappa_{ACSM}$  was due to the range of  $\kappa_{org}$  (0 to 0.2, see Eq. (3) and the related text).

#### **Classification by Trajectory Pathway**

In order to investigate the relationship between the trajectory pathways and the chemical composition of finemode aerosols, backward trajectories were classified into four types, based on the method of Iseki *et al.* (2010), according to the coastline where the air masses passed just before arriving at the NOTOGRO site (Fig. 7). Most air masses were continental origin, however, 42% of air masses passed over the Japanese islands (labeled as JPN in Fig. 7) after leaving the Asian continent. The remaining air masses passed over Russia (RUS), northeast China (NCH) and central China (CCH) before crossing the Sea of Japan and arriving at the NOTOGRO site (Fig. 7). The trajectory classified as CCH is characterized by crossing the coastline of the Asian continent below 40°N. The appearance frequencies of RUS, NCH and CCH were 17%, 27% and 13%, respectively (Table 2). The temporal variations of the trajectory pathways are also indicated at the top of Fig. 6.

In Table 2, total mass concentrations, mass ratios and  $\kappa_{\rm CCN}$  are summarized according to trajectory pathway. There is a clear difference in the total mass concentrations among the trajectory pathways. The higher mass concentrations are observed during the period classified as NCH (6.8 µg m<sup>-3</sup>) or CCH (7.7 µg m<sup>-3</sup>), and the lower mass concentrations occur during the periods of RUS (4.2 µg m<sup>-3</sup>) or JPN (3.6 µg m<sup>-3</sup>) (Fig. 6 and Table 2). The mean ratio of organics to

Loootion	Concord	Cito truco		Averag	e concentrations	fo ( <sup>-3</sup> ) of	NR-PM <sub>1</sub> und	ler ambient	conditions
LOCATION	DCdSUII	addi anc	Organics	Sulfate	Ammonium	Nitrate	Chloride	Total	Reference
Beijing, China	Su	Urban	20.0	9.0	8.0	12.4	0.5	49.9	Sun <i>et al</i> . (2012)
Beijing, China	M	Urban	34.4	9.3	8.6	10.9	3.5	66.8	Sun <i>et al</i> . (2013)
Guangzhou, China	Su	Urban downwind	16.1	12.8	6.1	1.8	0.9	37.8	Rose et al. (2011)
Tokyo, Japan	W (2003)	Urban	6.7	2.5	2.2	3.1	0.5	15.3	Takegawa <i>et al.</i> (2006)
Tokyo, Japan	Su	Urban	5.7	3.2	1.8	1.0	0.09	12.7	Takegawa et al. (2006)
Tokyo, Japan	Α	Urban	7.1	1.8	1.3	1.0	0.1	11.9	Takegawa <i>et al.</i> (2006)
Tokyo, Japan	W (2004)	Urban	5.8	1.7	2.3	2.8	0.5	14.0	Takegawa <i>et al.</i> (2006)
Jeju Island, Korea	Sp	Rural/Remote	3.5	3.1	1.5	0.5	$NA^b$	$8.6^c$	Topping <i>et al.</i> (2004)
Okinawa Island, Japan	all	Rural/Remote	1.1	3.8	0.8	0.1	0.0	5.8	Miyoshi et al. (2013)
Okinawa Island, Japan	Sp	Rural/Remote	2.2	6.4	1.3	$\mathrm{NA}^b$	$NA^b$	$6.6^{d}$	Takami <i>et al</i> . (2007)
Fukue Island, Japan	Sp	Rural/Remote	5.0	4.8	1.6	0.6	0.07	11.0	Takami <i>et al</i> . (2005)
NOTOGRO	А	Rural/Remote	2.7	1.9	0.6	0.2	0.05	5.4	This Study
<sup>a</sup> Sp, Su, A and W indicate s	pring, summer,	autumn and winter, re	spectively; <sup>b</sup> N	Vot availabl	e;				
<sup>c</sup> Organics + Sulfate + Amm	onium + Nitrat	te; <sup><math>d</math></sup> Organics + Sulfate	+ Ammoniur	'n.					



**Fig. 7.** Examples of classified airmass trajectories for (i) RUS, (ii) NCH, (iii) CCH and (iv) JPN during the observation period. The trajectories are colored according to their altitude.

sulfate mass concentrations (Org/SO<sub>4</sub>) throughout the entire observation period  $(1.6 \pm 1.0)$  was higher than at other rural/remote sites in East Asia (Table 1), however, the values of Org/SO<sub>4</sub> also varies with trajectory pathway. The value of Org/SO<sub>4</sub> was low during the periods of CCH (1.2) and NCH (1.3), and the large Org/SO<sub>4</sub> was observed during the period of RUS (2.2). The values of  $f_{44}$  were 0.17, 0.20, 0.17 and 0.18 during the periods of RUS, NCH, CCH and JPN, respectively (Table 2), indicating that the organic aerosols were highly oxygenated regardless of the trajectory pathway.

The larger  $\kappa_{\rm CCN}$  were observed during the period classified as CCH (0.37 and 0.34 under the SS conditions of 0.13% and 0.82%, respectively), which is consistent with the small value of Org/SO<sub>4</sub> during the same period (Table 2). However, Org/SO<sub>4</sub> did not always correspond with  $\kappa_{CCN}$ ; the  $\kappa_{CCN}$ were almost the same level between the periods of RUS and NCH although there was a large difference in Org/SO<sub>4</sub> values (Table 2). This might be caused by a difference in organic species (even if the organic aerosols observed in both periods were highly oxygenated) and/or mixing states of ambient aerosols. During the period of CCH, the  $\kappa_{\rm CCN}$ were relatively constant (0.34 to 0.37) with SS conditions when compared with the averaged  $\kappa_{CCN}$  shown in Fig. 5. This indicates that chemical composition of the aerosol observed in the CCH period was rather uniform with respect to particle size. In contrast,  $\kappa_{\rm CCN}$  varied significantly during the periods of RUS, NCH and JPN periods, suggesting that relatively fresh, less hygroscopic organics were included in the size range of the ultra-fine fraction ( $d_{\rm m} < 50$  nm).

#### Growth of Cloud Droplet (Droplet Activation Kinetics)

The temporal variations of  $D_{\text{ambient}}$  for four different SS conditions are shown in Fig. 6(d). As expected, droplet sizes depend primarily on SS, and were similar to the  $D_{\text{AS}}$  under

Trajectory pathway	Appearance frequency (%)	Total mass concentration $(\mu g m^{-3})$	Org/SO <sub>4</sub>	$f_{44}$	$\binom{\kappa_{\rm CCN}}{\rm (SS=0.13\%)}$	$\binom{\kappa_{\rm CCN}}{\rm (SS=0.81\%)}$
RUS	17	$4.2 \pm 2.0$	$2.2 \pm 1.2$	$0.17 \pm 0.03$	$0.34\pm0.08$	$0.19 \pm 0.06$
NCH	27	$6.8 \pm 2.3$	$1.3 \pm 0.4$	$0.20\pm0.04$	$0.34\pm0.03$	$0.23\pm0.08$
ССН	13	$7.7 \pm 4.4$	$1.2 \pm 0.5$	$0.17 \pm 0.05$	$0.37\pm0.02$	$0.34\pm0.05$
JPN	42	$3.6 \pm 1.8$	$1.5 \pm 0.8$	$0.18\pm0.06$	$0.32\pm0.08$	$0.22\pm0.07$

**Table 2.** Summary of  $\kappa_{\rm CCN}$ , mass concentrations and mass ratios according to trajectory pathways

every SS condition. The mean  $D_{\text{ambient}}$  (mean ± standard deviation) were 1.47 ± 0.09, 2.01 ± 0.06, 4.74 ± 0.08 and 5.88 ± 0.11, respectively, under the SS conditions of 0.13%, 0.25%, 0.52% and 0.81%. The temporal variation of the ratio of  $D_{\text{ambient}}/D_{\text{AS}}$  (i.e., size of droplets activated from ambient aerosols relative to that from (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is shown in Fig. 6(e) for better comparison. The ratios were close to 1 at higher SS conditions (i.e., 0.52% and 0.81%), indicating that the chemical composition of the CCN had an insignificant effect on the initial cloud droplet growth under an abundant supply of water vapor. However, the  $D_{\text{ambient}}$  was consistently smaller than  $D_{\text{AS}}$  at lower SS conditions (i.e., 0.13% and 0.25%) and their ratios showed large temporal variations (Fig. 6(e)).

The periods that the droplets growth were significantly inhibited as compared to those of pure (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were observed (e.g., 1500 LT Oct 9 to 0300 LT Oct 11, and 2100 LT Oct 23 to 0100 LT Oct 25; hereafter referred to as Event 1 and Event 2, respectively) (Fig. 6). The trajectory pathways during Event 1 and 2 were classified as JPN and RUS/NCH, respectively. These periods are characterized by the small  $D_{\text{ambient}}/D_{\text{AS}}$  lasting for more than 24 hours, and the values were less than  $-1\sigma$  of the mean  $D_{ambient}/D_{AS}$ (0.88) at SS = 0.13%. The measured  $D_{\text{ambient}}/D_{\text{AS}}$  were as low as  $0.85 \pm 0.04$  and  $0.80 \pm 0.02$  for Event 1 and Event 2, respectively (Fig. 6(e)). Bougiatioti et al. (2011) reported that ratios of the sizes of droplets activated from ambient aerosols to those from NaCl were 0.93 to 1 under the SS conditions of 0.21% to 0.73%. Although the analysis method and chemical composition of CCN were not completely the same, the  $D_{\text{ambient}}/D_{\text{AS}}$  observed in this study were considerably smaller compared to the ratios reported previously (Bougiatioti et al., 2011).

There are several factors that can control the cloud droplet growth: SS, size, and chemical composition of CCN. In our experiment, SS were kept constant, and the diameters of the CCN were also confined to the range of 160 to 240 nm when  $D_{\text{ambient}}$  were compared to  $D_{\text{AS}}$ . Therefore, the chemical composition of the CCN was possibly the cause for the temporal variation of  $D_{\text{ambient}}/D_{\text{AS}}$  observed here. The organic mass fraction accounted for 49% of the submicrometer aerosols on average; however, the periods of Event 1 and 2 were characterized by the highest organic mass fractions of the observation period (Fig. 6(b)). The  $D_{\text{ambient}}/D_{\text{AS}}$  plotted as a function of the organic mass fraction for SS conditions of 0.13% and 0.25% are shown in Fig. 8. As shown in Fig. 8,  $D_{\text{ambient}}/D_{\text{AS}}$  tends to be smaller in the presence of a large organic mass fraction in the CCN. In addition, the plots of  $D_{\text{ambient}}/D_{\text{AS}}$  during Event 1 and 2 are



**Fig. 8.**  $D_{\text{ambient}}/D_{\text{AS}}$  plotted against organic mass fraction (%) derived by ACSM, under SS conditions of (a) 0.13% and (b) 0.25%.

found at the bottom right of the scatter plots, and indicate that the significant decrease in the droplet size was caused by the large mass fraction of organics in the activated CCN. Although the organic aerosols observed in the NOTOGRO site were highly oxygenated in terms of  $f_{44}$ , the low values of  $\kappa_{\rm CCN}$  were observed during Event 1 and Event 2 under all SS conditions (Fig. 6(c)). During the periods, the contribution of less-hygroscopic (or fresh) organics to the aerosol mass might be relatively higher than aging one. These results suggest that the initial growth of the cloud droplet during Event 1 and 2 was inhibited by less-hygroscopic organics.

### **CONCLUDING REMARKS**

Simultaneous measurement of the size-resolved CCN activity and bulk chemical composition of the fine-mode aerosols were conducted at Noto Peninsula, Japan, which is located in the downwind region of the northeast part of the Asian Continent. Parameters related to the CCN activity of the aerosols were obtained at high temporal resolution based on the analysis of the CCN efficiency spectra. The slope of the CCN efficiency spectra for ambient aerosols was

not as steep as that for pure  $(NH_4)_2SO_4$  particles, indicating heterogeneity in the mixing states of the ambient aerosol. The hygroscopicity parameter  $\kappa$ , derived by the CCN activation diameter, suggested that organics contributed to the aerosol mass, especially in the size range of less than 100 nm. Based on the observation, ambient aerosols observed at the NOTOGRO site during autumn are characterized by: 1) large contribution of organic aerosols to the aerosol mass; and 2) dominance of highly oxygenated (aged) organic aerosols compared to other remote sites in East Asia. However, the aerosols with small  $\kappa$  values (i.e., lesshygroscopic aerosols) were observed during the periods that air masses came from Russia, northeast China or Japan.

Our results clearly indicate that representing CCN activity simply by a single and large  $\kappa$  value (as previously reported) irrespective of the particle size and air mass origin may lead to an overestimation of CCN number concentrations in the Asian outflow. This adds further value to the longterm aerosol monitoring at multiple locations in East Asia, i.e., downwind regions of not only highly-industrialized area but also less industrialized area, for better predicting CCN number concentrations over East Asia.

An apparent suppression of the cloud droplet growth was observed under the low SS conditions during the periods of high organic mass concentrations, suggesting that relatively fresh, less-hygroscopic organics affected the droplet activation kinetics. Identification of the organic species that contribute to the suppression of droplet growth remains to be solved in the future studies.

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