Hygroscopicity and cloud condensation nucleus activity of marine aerosol particles over the western North Pacific

Michihiro Mochida,1 Chiharu Nishita-Hara,1 Hiroshi Furutani,2 Yuzo Miyazaki,3 Jinyoung Jung,2 Kimitaka Kawamura,3 and Mitsuo Uematsu2

Received 14 July 2010; revised 12 October 2010; accepted 27 October 2010; published 19 March 2011.

1] Hygroscopic growth of aerosol particles at 85% relative humidity and the number fraction of cloud condensation nuclei (CCN; 0.42%, 0.23%, and 0.10% supersaturation) as a function of dry diameter (24.1–359 nm) were measured simultaneously on board R/V Hakuho-Maru over the western North Pacific during August–September 2008. Highly hygroscopic and unimodal growth distributions were observed, except for aerosols, which showed lower hygroscopic growth over the northern Pacific. The measured particle hygroscopicity, CCN activation diameters, and chemical composition data suggest the dominance of internally mixed sulfate aerosols. Backward air mass trajectory analysis exhibits an intrusion of free tropospheric aerosol, which was likely influenced by Kasatochi’s volcanic plume and which was linked to the low-hygroscopicity event. Frequent observation of the Hoppel minimum suggests that in-cloud processing over the Pacific enhanced and/or maintained the high hygroscopicity of accumulation mode particles. The CCN activation diameters predicted from median hygroscopic growth factors (g_median) agreed well with those determined from the CCN efficiency spectra, without assuming surface tension reduction caused by organics or enhancement of bulk hygroscopicity at high RH caused by sparingly soluble or polymeric compounds. The CCN spectra predicted from g_median and measured CCN activation diameters suggest that the high CCN activities of particles over the North Pacific are sustained by high hygroscopicity, while sporadic changes of aerosol origins produce the diversity of the aerosol properties.


1. Introduction

[2] Atmospheric aerosols over oceans, which cover most of the Earth’s surface, play important roles in global climatic and meteorological processes [Albrecht, 1989; Fitzgerald, 1991]. Chemical and physical properties of marine aerosols are expected to differ from those of continental aerosols because of their different emission sources [e.g., O’Dowd et al., 2004; Clarke et al., 2006], precursors and formation pathways, and atmospheric transport [e.g., Clarke et al., 1998; Shaw et al., 1998]. Although many aerosol properties are related to their roles in climatic and meteorological processes, our knowledge of marine aerosol properties remains limited, which might be attributable in part to the difficulty of making measurements of aerosols over the ocean. In particular, to elucidate the influence of marine aerosol particles on the radiative budget and the cloud droplet formation precisely, detailed information about their hygroscopicity and cloud condensation nucleus (CCN) activity is necessary, in addition to their number concentrations and size distributions.

[3] The North Pacific Ocean constitutes a large fraction of the world’s oceans. The aerosols over it have been studied in view of their hygroscopicity and CCN activity as well as the temporal and spatial distributions of their number concentrations, chemical composition, and optical properties [e.g., Huebert et al., 2003], which shed light on the complexity of their sources and processing. For example, the remote Pacific area was found to be a source of new particles formed by the vertical transport of reactive gases to the free troposphere, producing sulfuric acid (SA), with subsequent nucleation [Clarke et al., 1998]. Furthermore, the release of sea salts is regarded as an important source of ultrafine particles [Clarke et al., 2006]. The North Pacific is particularly influenced by the seasonal outflows from Asia, which transport gaseous and particulate anthropogenic components as well as dust particles to the remote atmo-
Regarding the hygroscopic properties of marine aerosol particles, reports have described aerosols over the western North Pacific [Massling et al., 2007] and over the eastern North Pacific [Berg et al., 1998] and other oceanic regions [Swietlicki et al., 2000; Zhou et al., 2001; Majling et al., 2003; Tomlinson et al., 2007; Good et al., 2010]. In a study by Massling et al. [2007], hygroscopic growth factors of the western North Pacific aerosol particles in the marine boundary layer (MBL) were investigated in spring, the season during which Asian continental outflow to the Pacific is substantial. The CCN activity of aerosol particles over the north Pacific has been subjected to analyses only recently. Such studies have mainly examined aerosols in the eastern North Pacific [Roberts et al., 2006; Furutani et al., 2008; Shinozuka et al., 2009]. Over the western North Pacific region, the number concentration levels of CCN are being clarified [e.g., Ishizaka et al., 1995; Matsumoto et al., 1997; Nagao et al., 1999].

Extensive studies of hygroscopic properties and the CCN activity of aerosol particles over the western part of the North Pacific region are crucially important. Future studies must characterize those properties for the periods during which the continental outflow is weak and must interpret the CCN number concentrations based on the particle properties. For this study, we performed shipboard measurements of aerosol hygroscopicity and CCN activity in the MBL over the western North Pacific region during the season when Asian outflow to the Pacific was expected to be slight. This field investigation was conducted using a state-of-the-art approach using size-segregated measurements of hygroscopic growth factors and the CCN number fraction inferred from high-resolution particle diameter data. These size segregation measurements provide detailed information related to these aerosol properties, as demonstrated using the same method in Okinawa, Japan [Mochida et al., 2010] as well as by field measurements of size-resolved CCN fractions [e.g., Dusek et al., 2006; Kuwata et al., 2008; Gunthe et al., 2009]. Because the studied area was distant from major continental source regions of aerosols such as East Asia, Southeast Asia, and North America, the aerosols in the area were expected to be influenced by marine and free tropospheric sources as well as highly aged aerosols that were transported over long ranges. Characteristics of the physical and chemical properties of marine aerosol particles are discussed in view of air mass origins, potential sources and processes, and the relation to the number-size distributions and CCN concentrations. The subject of the present discussion includes the plume from the eruption of Kasatochi volcano.

2. Experiments

2.1. Hygroscopicity and CCN Activity Measurements

The particle hygroscopic growth factors and the fraction of CCN to condensation nuclei (CN) as a function of dry mobility diameter ($d_{p,dry}$) were measured simultaneously using a hygroscopicity tandem differential mobility analyzer (HTDMA)–CCN counter (CCNC) system over the western Pacific on board R/V Hakuho-Maru during the KH-08-2 cruise (leg 1, northwestern North Pacific; leg 2, western North Pacific). To warrant consistent quality of data for the present analyses, we particularly examine data obtained during the leg 2 cruise from Kushiro to Tokyo, Japan: a long time series of HTDMA–CCNC data was collected without major instrumental problems, with calibration results of HTDMA and CCNC before and after the leg. Figure 1 presents the cruise track and the locations of the hygroscopicity and CCN measurements. The studied area was 10°N to 44°N, which covers the subarctic to subtropical region. The time period of data subjected to analyses extends from ~0300 UT, 24 August (day of year (DOY) 237), to ~0300 UT, 12 September (DOY 256) 2008.

For measurement of particle hygroscopic growth and CCN number fractions, atmospheric aerosol was aspirated at a flow rate of 17 L min⁻¹ on the upper deck. The inlet was placed at the front edge of the upper deck facing the bow to avoid sampling of the ship exhausts. The aerosol was drawn to the laboratory beneath the deck, passed through the PM₁ cyclone, and introduced to the HTDMA-CCNC system at a flow rate of 0.65 L min⁻¹. The system was based on one described elsewhere [Mochida et al., 2010] (hereinafter, the citation of Mochida et al. [2010] includes their auxiliary materials). Briefly, aerosol particles dried in diffusion dryers were classified in the first DMA (DMA1, <5% RH) of the HTDMA. The hygroscopic growth of the exiting aerosol after humidification at 85% RH was measured using the second DMA (DMA2) and a condensation particle counter (CPC) in the scanning mobility particle sizer (SMPS) mode. The major modifications from the work of Mochida et al. [2010] include the use of CPC with a water removal function (Model 3775; TSI Inc.) downstream of DMA2, the absence of a Nafion dryer between DMA2 and the CPC, and the use of high-voltage units (DMS-10K05N/24; Max-Electronics Co. Ltd.) for DMA2 as well as DMA1. Part of the aerosol classified in the DMA1 was also introduced to a CCN counter (CCN-100; Droplet Measurement Technologies) and another CPC to measure the concentrations of
condensation nuclei (CN) and CCN. Different from the work of Mochida et al. [2010], an ultrafine condensation particle counter (UCPC, Model 3025A, TSI Inc.) was used to measure the concentrations of CN. Operation of the UCPC without a wick was possible, and was confirmed as acceptable, as described by Mochida et al. [2010]. The voltage applied to DMA1 was changed automatically every 5 min to measure the hygroscopic growth and the concentration ratios of CCN to CN for particles with different mobility diameters \(d_{\text{p,dry}}\). Different sets of 34 sizes from 24.1 to 359 nm were applied to the HTDMA-CCNC measurement depending on the supersaturation (SS) conditions in the CCNC (0.42, 0.23 and 0.10%) in 3 h. The particle sizes covered the range within which most CCN are commonly present.

Before and after the atmospheric measurements, ammonium sulfate (AS) particles were introduced to the HTDMA-CCNC on site to adjust the sizing of DMA1 and DMA2, and to validate the measurements of particle hygroscopic growth. The hygroscopic growth factor \(g\), which is defined by the ratio of the mobility diameter at \(\sim 85\%\) RH relative to that at \(<5\%\) RH, were measured for pure AS particles to be, for example, 1.51 \pm 0.02, 1.55 \pm 0.01, and 1.60 \pm 0.03 at \(d_{\text{dry}}\) of 49.6, 102, and 209 nm, respectively. The \(g\) values agreed well with those calculated using the Köhler model described in section 2.6 (1.55, 1.57, and 1.59 at 49.6, 102, and 209 nm, respectively). Details in the data inversion procedure to derive \(g\) from raw HTDMA data are presented by Mochida et al. [2010]. The CCN efficiency spectra, which are the \(d_{\text{NCN}}/d_{\text{CN}}\) ratios as a function of \(d_{\text{dry}}\), \(N_{\text{CCN}}\), atmospheric number concentration of CCN; \(N_{\text{CN}}\), atmospheric number concentration of CN), were calculated considering the presence of multiple charged particles [Mochida et al., 2010]. The CCN efficiency spectra were then fitted with the cumulative distribution function [Rose et al., 2008].

\[
\frac{d_{\text{NCN}}}{d_{\text{CN}}} = \frac{1}{2} \left( 1 + \text{erf} \left( \frac{d_{\text{dry}} - d_{\text{act}}}{b \sqrt{2}} \right) \right) \tag{1}
\]

In that equation, the diameter at which \(d_{\text{NCN}}/d_{\text{CN}}\) reached 50% of the maximum is defined as the CCN activation diameter \(d_{\text{act}}\). According to the method used by Mochida et al. [2010], the SS conditions in the CCNC were determined using the Köhler equation with \(d_{\text{act}}\) of pure AS particles, which was derived from the calibration experiments on the ship. Note that the results obtained at the low SS (0.10%) possibly have larger uncertainty because of the difficulty in differentiating activated from nonactivated droplets [Roberts and Nenes, 2005; Mochida et al., 2010].

### 2.2. Aerosol Size Distributions and Number Concentrations

The number-size distributions of atmospheric aerosols \((d_{\text{NCN}}/d_{\text{log}d_{\text{p,dry}}})\) were calculated from the UCPC particle counts, based on the principle of the differential mobility particle sizer (DMPS). The \(d_{\text{NCN}}/d_{\text{log}d_{\text{p,dry}}})\) values in the resolution of 64 channel/decade were calculated by interpolation of particle number concentrations downstream of DMA1 at 16 different sizes from 24.1 to 359 nm, with subsequent consideration of the DMA transfer function [Stolzenburg, 1988], charging efficiency [Wiedensohler, 1988; TSI Inc., 2006] and diffusion loss of particles in the sampling line [Soderholm, 1979]. Aerosol number concentrations measured using a water-based CPC (WCPC, Model 3785; TSI Inc.) were used for comparison with the DMPS-derived number size distributions. The aerosol for the WCPC was aspirated (6 L min\(^{-1}\)) at the front edge of the upper deck and transferred through a sampling line. Based on post calibration of the WCPC, a 30% decrease in the counting efficiency was corrected.

### 2.3. Aerosol Chemical Composition

Particulate sulfate (PM\(_{1}\)) and nitrate (PM\(_{2.5}\)) were monitored continuously using a sulfate monitor and a nitrate monitor (Series 8400S ambient particulate sulfate monitor, Series 8400N ambient particulate nitrate monitor; Rupprecht and Patashnick Co., Inc.) on the upper deck. Concentrations of organic carbon (OC) and elemental carbon (EC) in all suspended particles (TSP) were determined through carbon analysis of aerosol samples collected on quartz fiber filters using a high-volume air sampler every 0.5–1 days. During the sample collection, the power supply of the sampler was controlled using a wind speed and direction monitor so that aerosols were collected when the wind speed and direction were >5 m s\(^{-1}\) and within 60° from the bow, respectively. The OC and EC were quantified using a carbon analyzer (Sunset Laboratory Inc.) with the protocol described by Miyazaki et al. [2009]. The concentrations of OC and EC were presented for samples whose concentrations were greater than the mean plus 3 standard deviations (SD) (5 ng C m\(^{-3}\)). Because the EC concentrations were below the blank level for most samples and because those quantified were low (<7 ng C m\(^{-3}\)), they are not presented in this paper.

### 2.4. Data Screening

To omit measurement data that were influenced by the ship exhaust, data collected when the relative wind direction (RWD) was within 60° from the bow and when relative wind speed (RWS) was ≥3 m s\(^{-1}\) were used for analyses. The HGF measurements were conducted every 5 min. Hygroscopic growth data collected during the time \(\text{bin}(\text{s})\) when RWD or RWS was out of the range described above were omitted; those collected during three more time bins (one before and two after the corresponding \(\text{bin}(\text{s})\)) were also omitted, in part to avoid possible sampling of the ship exhaust stagnating around the ship. Bias in the time of each PC for data acquisition of up to a few minutes was used without correction. However, the differences of the clocks were treated appropriately to choose the effective measurement time of the CCN counter. The sequence of the \(d_{\text{NCN}}/d_{\text{CN}}\) measurement was repeated every 3 h; sets of the 3 h data were omitted when RWD or RWS was out of the criteria during a part of the 3 h period and additional 5 min before it. Hygroscopic growth factors \(g\) when the RH measured at the inlet and outlet of the DMA2 sheath air as well as that at the inlet of the DMA2 sample air were 83% < \(RH < 87\%\) were used for analyses. Unrealistic zero concentration values recorded by the WCPC were omitted. Screening based on RWD and RWS were performed for the 10 min data of sulfate and nitrate, where data in the neighboring bins were omitted, too. Zero concentration of sulfate after the maintenance was also omitted. The accepted
10 min data of sulfate were further averaged to calculate the 3 h averages.

### 2.5. Trajectory Analysis

Backward air mass trajectory analysis was performed using the NOAA Air Resources Laboratory (ARL) HYSPLIT transport and dispersion model (http://www.arl.noaa.gov/ready.html) with NCEP/NCAR reanalysis data. The trajectories were calculated for air masses that reached 500 m (amsl) above the R/V Hakuho-Maru 1 h after the 3 h measurement period. Atmospheric pressure, relative humidity, and mixing depth along the trajectories were also used for analyses.

### 2.6. Thermodynamic Models

A core-shell model, in which a particle is assumed to be composed of an insoluble core and a soluble shell, was used to predict the critical SS of particles with specific g. The hygroscopic growth of particles under subsaturated and supersaturated water vapor conditions was calculated based on a Köhler equation as described by Mochida et al. [2010] on the assumption that the solute is either AS, ammonium bisulfate (ABS), or SA. The temperatures at which the hygroscopic growth at 85% RH and the CCN activation were measured were assumed to be 301 and 303 K, respectively. The calculations were basically based on the equations given by Brechtel and Kreidenweis [2000]; the molality-dependent osmotic coefficients were calculated using a Pitzer equation with parameters reported by Kim et al. [1993].

Figure 2. Time series of (a) particle number concentrations measured using the DMPS (24.1–359 nm, triangles) and the WCPC (circles) and (b) absolute and (c) normalized number-size distributions of aerosol particles calculated from the DMPS data. Data points that are off of the y scale (from WCPC) were presumably caused by the ship’s exhaust and are not presented. Time periods 1, 2, and 3 are presented with horizontal arrows at the top of Figure 2a (see the text for details).
an insoluble core, the g values of pure inorganic salts (AS, ABS, and SA) were estimated based on the Köhler model described above.

3. Results and Discussion

3.1. Aerosol Number Size Distribution

[14] Figure 2 presents time series of the particle number concentrations derived from the DMPS (24.1–359 nm, with screening based on RWD/RWS) and the WCPC (w/o RWD/RWS screenings), and the absolute and normalized number size distributions of the MBL aerosols. The periods with sharp increases in the particle number concentrations measured using the WCPC were mostly excluded from the effective periods of the DMPS-derived distributions, indicating a successful screening for the ship’s exhaust. Figure 2a shows that the number concentrations were high during DOY 237–240 (period 1) and DOY 252–255 (period 3; 24 h averages from DMPS data: >295 particle cm\(^{-3}\)). The influence of the eruption of Kasatochi volcano during period 1 is discussed later. In period 3, influence of the plumes from the Hawaiian volcano is possible, as discovered in the work of K. Eguchi et al. (manuscript in preparation, 2011). In contrast, the concentrations found in the middle of the measurement period (period 2; DOY 241–251) were persistently low (24 h averages from DMPS data: <204 particle cm\(^{-3}\)), presumably representing typical remote marine aerosols in the western Pacific. Bimodal distributions with Aitken and accumulation modes were observed particularly when the particle number concentrations were low (Figure 2c). The increases in the number concentrations during periods 1 and 3 were associated with large increases in the concentrations of accumulation mode particles and less clear bimodal characteristics (Figure 2b). Note that the bimodal characteristic is observed for sizes of 24.1–359 nm; the possible presence of an additional mode in a smaller size range [Ehn et al., 2010] is not analyzed in this study.

3.2. Average Characteristics of Particle Hygroscopicity and CCN Activity

[15] Figures 3a and 3b portray contours of the averages of absolute particle and normalized particle number concentrations versus \(d_{\text{dry}}\) and g. On average, the distributions of g in both Aitken and accumulation mode size ranges were unimodal, with a maximum mainly at g of 1.5–1.6. The normalized distribution (Figure 3b) shows no abrupt change in the distribution of g between Aitken and accumulation mode size ranges, although they appeared as two distinct modes (Aitken and accumulation modes) in view of the particle number concentrations (Figure 3a). The observed aerosols are characterized by high hygroscopicity down to the size range of Aitken mode particles, given that Aitken mode particles studied by Su et al. [2010] for urban and pristine rain forest airs seem to distribute in the lower range of \(\kappa/C_{20}\). From individual hygroscopic growth factor distributions collected every 3 h, median values of g were calculated for \(d_{\text{dry}}\) and were fitted with a third-order polynomial function of \(\log d_{\text{dry}}\) (ranges of \(d_{\text{dry}}\); from 34.6 nm (0.23% and 0.10% SS) or 41.4 nm (0.42% SS) to 250 nm) to derive fitted median growth factors \(g_{\text{median}}\) [Mochida et al., 2010]. Histograms of \(g_{\text{median}}\) for 50, 75, and 150 nm particles are presented in Figure 4. Here, 50 and 150 nm particles are
Figure 4. Frequency distributions of median growth factor $g_{\text{median}}$ for particles whose dry mobility diameters $d_{p,dry}$ were (a) 50 nm, (b) 75 nm, and (c) 150 nm. The values of hygroscopicity parameter $\kappa$ calculated from $g_{\text{median}}$ at 85% RH ($\kappa_{85\text{,median}}$) are shown by the top axes. The inverted triangles show $g$ values estimated for pure AS (gray triangles), ABS (open triangles), and SA (black triangles) using the Köhler model. Estimated ranges of $g$ for particulate organics are presented as horizontal gray lines (see the text for details).

selected as examples of Aitken and accumulation mode particles, respectively, whereas 75 nm particles represent those between the two modes. As Figure 4 shows, $g_{\text{median}}$ is distributed within a narrow range irrespective of $d_{p,dry}$. The $g_{\text{median}}$ values and the corresponding hygroscopicity $\kappa$ ($\kappa_{85\text{,median}}$) were similar to those of pure AS and ABS and were lower than those of SA (Figure 4). Conversely, the observed $g_{\text{median}}$ and $\kappa_{85\text{,median}}$ were markedly higher than those of organics in atmospheric particles (ranges estimated from the results given by Jimenez et al. [2009] are shown by the horizontal bars in Figure 4). The result in Figure 4 shows that a large fraction of observed particles in both Aitken and accumulation modes was composed of highly hygroscopic water-soluble components such as sulfate. Because the $\kappa$ values of different components can be approximated as additive, Figure 4 further suggests that the volume fraction of organics can be comparable to sulfate if most of the sulfate is in the form of SA. It is noteworthy, however, that even with SA, the contribution of organics to the particle hygroscopic growth is small because of their smaller $\kappa$ than that of sulfate. Table 1 presents the mean and SD of $g_{\text{median}}$ and corresponding $\kappa_{85\text{,median}}$ calculated for five selected diameters.

Table 1 presents the mean and SD of $g_{\text{median}}$ and corresponding $\kappa_{85\text{,median}}$ calculated for five selected diameters.

### 3.3. Temporal and Spatial Variations of Hygroscopicity, CCN Activity, and the Chemical Composition of Marine Aerosols

[17] Figures 6a and 6b present time series of the latitude of the ship’s location and the concentrations of sulfate, nitrate, and OC. Although the size ranges for the chemical analyses were much broader than that for the HTDMA-CCNC measurements, the composition data suggest that sulfate was the major water-soluble component down to the size range of 24.1–359 nm. This result explains the high hygroscopic growth factors and low CCN activation diameters. Figure 6b shows that substantial amounts of organics might also exist in 24.1–359 nm; that proportion depends on the organic mass (OM) to OC ratios as well as the concentrations of OC. Figure 6c presents the temporal variation of $g_{\text{median}}$ for 50, 75, and 150 nm particles. Irrespective of the particle size, $g_{\text{median}}$ was lower on DOY 238–239, when the ship was in the subarctic region (Figure 6a); values were persistently high during the remainder of the time period. During the low $g_{\text{median}}$ event, increased concentrations were observed for sulfate and OC (Figure 6b). The fitted activation diameters $d_{act}$ from equation (1) under 0.42%, 0.23%, and 0.10% SS are presented in Figure 6d. Although the low-hygroscopicity event (DOY 238–239) was associated with the increase in $d_{act}$, their correlations to...
Figure 5. The CCN efficiency spectra at (a) 0.42%, (b) 0.23%, and (c) 0.10% SS. The mean of $dN_{CCN}/dN_{CN}$ and the ranges within SD are shown as open red circles and shaded areas, respectively. The CCN efficiency spectra measured for AS (mean ± SD) are shown for comparison (solid blue squares). The vertical green lines represent the activation diameters calculated for AS (dash-dotted lines), ABS (dotted lines), and SA (dashed lines) using the Köhler model. The hatched area shows estimated ranges of activation diameters for hypothetical pure organic particles (see the text for details).

Figure 6. Time series of (a) the latitude of the ship’s location; (b) concentrations of sulfate (PM$_1$), nitrate (PM$_{2.5}$), and OC (TSP); (c) $d_{median}$ at 50 nm (squares), 75 nm (triangles), and 150 nm (circles); (d) $d_{act}$ at 0.42% SS (circles), 0.23% SS (triangles), and 0.10% SS (squares) with the averages (dotted, dash-dotted, and dashed lines, respectively); and (e) $U_{10}$ estimated from the local wind speed (at approximately 20 m asl) averaged for 5 min from 1 min data and estimated accumulation rate of sea-salt particles in the MBL with 1 day averaged mixing depth from the HYSPLIT model.
The history of pressure along the trajectories in Figure 7b shows that air masses were transported mostly in the lower troposphere, except for the period of the low $g_{\text{median}}$ event in the subarctic region.

The results presented in Figures 3–7 provide insight into the composition and mixing state of observed aerosol particles. Because the continental primary particle sources were absent along the 10 day trajectories (Figure 7) and because the observations were conducted from summer to early autumn, new particle formation [Bigg et al., 1984], typically with SA, was probably an important source of the particles with high $g$. Sea salts on which secondary components (likely sulfate) condensed might exist, although the concentration of pure sea salts ($g$ of approximately 2.0) [Ming and Russel, 2001] was negligible on average (Figure 3). This inference is based on the result that the estimated accumulation rate of sea-salt particles in 24 h average mixing depths ($\geq$250 m) derived from the HYSPLIT model is as high as several tens of particles per cubic centimeter per day (Figure 6e), with estimation of $U_{10}$ from the measured mean wind speeds ($\sim$20 m asl) with a 1/7 power law and using sea-salt flux parameterization by Nilsson et al. [2001]. The negligible number fraction of particles near $g = 1$ in Figure 3 suggests that less hygroscopic components, such as EC, transported from continents were minor fractions, and that they were thickly coated with highly hygroscopic components. The negligibly low concentration of EC in TSP relative to sulfate in PM$_1$ supports this interpretation.

Irrespective of the origins of particles passing in and out of the oceanic region, the formation of sulfate by the oxidation of DMS might be an important process accounting for the observed high hygroscopicity. Vallina et al. [2007] estimated the contribution of biogenic CCN from DMS oxidation over the subtropical Pacific (10°N–40°N) as 30%. Moreover, Nagao et al. [1999] suggested, based on their long-term measurements of non-sea-salt (nss) sulfate and methane sulfonic acid (MSA) over Hahajima Island (142°10′E, 26°38′N), that most nss sulfate transported from northeastern and southeastern sectors originates from the DMS oxidation. Another possible contributor that is specific to the high particle number concentration periods is a volcanic plume, as described in section 3.1. Emissions of SO$_2$ and other gaseous and particulate matter and subsequent particle production might have caused the increases in the particle number and sulfate concentrations and controlled the observed hygroscopicity and CCN activity.

Although the observed unimodal distribution of $g$ is similar to, for example, that of marine aerosols over the southeastern Pacific [Tomlinson et al., 2007], an earlier hygroscopicity study over a similar region (northern Pacific and marginal seas off the coast of Asia) revealed multimodal characteristics [Massling et al., 2007]. The difference in results obtained by Massling et al. [2007] and our own results suggests that the number of hygroscopicity modes varies temporarily in the North Pacific region. Massling et al. [2007] report that some fraction of particles has $g$ of approximately 2.0 at 90% RH over the central North Pacific: they regard them as sea salts. The absence of highly hygroscopic sea salts in the present study is probably the result of calm weather conditions and low sea-salt emissions as a result of the presence of an anticyclone over the western North Pacific in summer. Moreover, different

---

1Auxiliary materials are available in the HTML. doi:10.1029/2010JD014759.
Figure 8. Particle number concentration \(n(\log d_{p,dry}, \log g)\) as a function of \(g\) and \(d_{p,dry}\) for the aerosol sample measured at DOY 238.8–238.9. The dashed red lines show contours of hygroscopicity parameter \(\kappa_{85}\). Solid contours show critical SS estimated using the \(\kappa\)-Köhler theory.

contribution of polluted air masses probably explain their different hygroscopic modes [Swietlicki et al., 2000]. Massling et al. [2007] conducted their measurements in spring, when strong Asian outflow occurs; we conducted our measurements from summer to early autumn, when the outflow was not substantial (Figure 7).

3.4. Low-Hygroscopicity Event in the Subarctic Region

[22] A remarkable event in view of the hygroscopic growth is the large depression of \(g_{\text{median}}\) on DOY 238–239 (Figure 6c). Figure 8 presents an example of the hygroscopic growth factor distribution during the event: the low \(g_{\text{median}}\) resulted from the presence of intermediately hygroscopic as well as highly hygroscopic particles. The large spread of \(g\) suggests a large abundance of components whose growth factor is smaller than that of sulfate. As shown in Figure 7b, backward air mass trajectories suggest the relation of this unique distribution of \(g\) to the distinctive air mass origin. The low \(g_{\text{median}}\) in the northern North Pacific (colors of the trajectories are purple-blue, \(\sim 40^\circ\)N) are associated with the entrainment of air masses from the free troposphere. This association applies also for 50 nm and 150 nm particles (Figure S1). The association of the increase in the sulfate concentration up to \(>7\ \mu g\ m^{-3}\) during the low \(g_{\text{median}}\) event (Figures 6b and 6c) indicates that the sulfate concentration was also linked to the descending air masses in the subarctic region.

[23] The plume of the eruption from Kasatochi volcano, Aleutian Islands (52.17\(^\circ\)N, 175.51\(^\circ\)W) on 7 August 2008 [Martinsson et al., 2009; Rix et al., 2009] might have caused an enhanced sulfate concentration and might lower \(g_{\text{median}}\) on DOY 238–239. A substantial amount of SO\(_2\) over the subarctic in the northern hemisphere was reported from satellite measurements conducted in late August [Clerbaux et al., 2009]. A plume of SO\(_2\), which is apparently of Kasatochi origin, reached Kamchatka Peninsula on DOY 231, as presented by the GOME-2 derived SO\(_2\) vertical column density in Figure 9a (reproduced from the image source at http://sacs.aeronomie.be/). Figure 9b depicts the calculated locations of air masses on DOY 231, for those reached over R/V Hakuro-Maru during the observation period. The markers with colors showing low \(g_{\text{median}}\) of 75 nm particles (e.g., \(g_{\text{median}} < 1.40\)) were at about 50–60\(^\circ\)N, the region near that with high column SO\(_2\) concentrations. Although the calculated locations of air masses corresponding to low \(g_{\text{median}}\) are off the plume, the trajectories in Figure 9b show that, in a few days after DOY 231, these air masses reached the region where the significant SO\(_2\) plume was observed (Figure 9a). Similarly, the concentrations of sulfate detected in the observation area were high in the cases of air masses that had been around 50–60\(^\circ\)N on DOY 231 and that arrived at the high SO\(_2\) region in a few days (Figure 9c). It is possible that the air masses transported to the measurement areas were influenced by the SO\(_2\) plume in Figure 9a, as a result of a possible descent of the part of the plume. The pressure of air masses depicted by the marker size was low for air masses with low \(g_{\text{median}}\), being consistent with the possible contribution of the volcanic plume that might have been transported at higher altitude. Although the large increase in highly hygroscopic sulfate is apparently contradictory to the lower \(g_{\text{median}}\), the observed hygroscopicity suggests that less hygroscopic components in addition to sulfate were highly abundant in the size range presented in Figure 8. Interestingly, Martinsson et al. [2009] reported a large abundance of carbonaceous component in the upper tropospheric and lower stratospheric aerosols in the Kasatochi’s volcanic plume over Europe. If the aerosol observed by Martinsson et al. [2009] is approximated as SA, ABS, or AS and organics with \(\kappa\) of 0–0.16 (Figure 4) and if the OC mass data are converted to the organic volume using the relation given by Aggarwal et al. [2007] (i.e., (organic mass/OC)/density of approximately 1.5), then the growth factor is estimated as 1.28–1.43 (\(\kappa_{85}\): 0.19–0.34). The estimated \(g\) values might explain the low hygroscopicity in Figure 8, although the estimate depends on the chemical form of the carbonaceous component detected by Martinsson et al. [2009].

[24] An unidentified source of organics in the free troposphere [Heald et al., 2005] is an alternative or complementary explanation for the observed low \(g_{\text{median}}\) event. For example, Heald et al. [2005] reported an OC/Sulfate ratio higher than 3 over the northwestern Pacific. On the assumption that OC reported by Heald et al. [2005] was slightly hygroscopic (\(\kappa\): 0–0.16), that sulfate was in the form of SA, ABS, or AS, and that the OC mass can be converted to the organic volume as explained above, the \(g\) value at 85% RH is estimated as \(\leq 1.12–1.32\) (\(\kappa_{85}\): 0.07–0.23) using \(\kappa_{85}\) calculated for SA, ABS, and AS particles without the Kelvin effect. As Figure 8 shows, the \(g\) and \(\kappa_{85}\) values are sufficiently low to explain the presence of particles showing lower hygroscopic growth factors. Moreover, the degree of formation might depend on chemical components therein if
such unknown organics are secondary. It is possible that secondary organic aerosol formation is favored in the Kasatochi’s plume, for example, because of enhanced oligomerization of organics under highly acidic conditions. It is noteworthy that increased concentration of the organics relative to sulfate was not evident from OC in TSP and sulfate in PM$_2.5$ (Figure 6b) during the low $g_{\text{median}}$ event, which suggests that organics were concentrated in small particles (24.1–359 nm) and that sulfates were abundant at >359 nm. Although the contribution of primary and secondary organics from marine biota [O’Dowd et al., 2004] on the lower $g_{\text{median}}$ over the highly productive North Pacific area (Figure 9a) is possible, that would fail to explain the large variation of $g_{\text{median}}$ when air masses were transported persistently over the North Pacific around DOY 238–239. The estimated sea-salt accumulation rates (Figure 6e) during the low $g_{\text{median}}$ event do not correlate with either $g_{\text{median}}$ or particle number concentrations, further ruling out the contribution of primary marine aerosols. Biomass burning particles, which commonly show intermediate hygroscopicity [e.g., Lee et al., 2006; Petters et al., 2009a] were presumably not important either, as inferred from the absence of a significant biomass burning event along the trajectories (Figure S2; map of MODIS hot spot/active fire data generated by FIRMS Web Fire Mapper [Justice et al., 2002; Giglio et al., 2003; Davies et al., 2009]).

### 3.5. In-Cloud Processing

[B25] Bimodal size distributions observed in many time periods (Figure 2b) suggest that in-cloud processing contributes to the observed high hygroscopicity and CCN activity of particles in the accumulation mode size range. The 24 h averaged size distributions exhibited a clear minimum between Aitken and accumulation modes on DOY 237, 240–246, and 250, at which the minima were less than half of the maxima between the two modes. Figure 10a presents examples of 24 h average number size distributions during 6 days. The minima in Figure 10a resemble a “Hoppel minimum” [Hoppel et al., 1986], which is believed to appear as a result of cloud droplet formation followed by the growth of accumulation mode particles attributable to aqueous phase processes and particle coagulation to the cloud droplet. Results show that the appearance of the Hoppel minimum was related to the history of RH in the air masses. Figures 10b and 10c present the cumulative time during which the RH in air masses were greater than 80% RH at 3, 7, and 10 days and the 3, 7, and 10 day averages of RH, respectively. Data shown were calculated using the HYSPLIT model; the data are used as proxies for the presence of clouds along the trajectories. In Figure 10b, the long cumulative time at >80% RH and high RH appeared mainly during periods when the minimum was less than half of the maximum in Aitken and accumulation modes (horizontal arrows), suggesting a connection between the minimum and in-cloud processing. Although clouds are formed locally at >100% RH, cloud formation might correlate to the subsaturated RH conditions along the trajectories, given the limited spatial resolutions of the meteorological data and the horizontal and vertical uncertainties of the trajectories. As Figures 2c and 10 show, some of the aerosols had weaker bimodal size characteristics; the aerosols might also have been influenced by in-cloud processing, but the process...
predicted from the Altieri et al. – dd calculated using the and could be lower values were used to predict CCN activa-
reasonably agrees –/C20 if organics in polymeric forms absorb water and d g Petters et al.
accumulation mode particles and formation of the Hoppel
cloud droplets might also have contributed to the growth of Pandis
dominant formation pathways of sulfate [e.g., 1997]. Coagulation of interstitial particles with
enhanced minimum. Because new particle formation from SA is suggested in the free troposphere [Clarke and Kapustin, 2002], it is reasonable to infer that free tropospheric aerosol particles that coagulate with cloud droplets were rich in sulfate and that the coagulation added sulfate to accumulation mode particles. The high hygroscopicity of Aitken mode particles observed in the MBL (Figures 4 and 5c) is consistent with this explanation. Conversely, in-cloud formation of SOA was unlikely to be the main contributor to the particle hygroscopicity because, although in-cloud formation of oxalic acid [e.g., 2003] and other small molecules might engender high hygroscopicity and CCN activity, the oligomerization of organics in cloud droplets [e.g., 2006] might reduce it because such large molecules are presumably not highly hygroscopic [e.g., 2009b].

3.6. Assessment of CCN Activation Based on the Köhler Theory

[27] The g_median values were used to predict CCN activation diameters (d_{act,HTDMA}) based on a core-shell model with a soluble core of either SA, ABS, or AS, to diagnose the relation between hygroscopic growth and CCN activation, and to assess a possible lowering effect of organics on surface tension. Here, the comparison is also made using d_{act,HTDMA} predicted from the κ- Köhler theory. Figure 11 presents a relation between measured and predicted activation diameters based on the CCN data collected at 0.42%, 0.23%, and 0.10% SS. Irrespective of the soluble fraction assumed and the model used, d_{act,HTDMA} reasonably agrees to the measured d_{act}. Small differences between different model calculations arise from the fact that, whereas κ- Köhler theory assumes gas/particle water partitioning that is analogous to that of ideal solution, the core-shell model includes the assumption of the nonideality of the different kinds of sulfate solutions. An important implication of this closure is that the possible lowering effect of organics on surface tension is small for the aerosol particles over the western North Pacific. This result contrasts against those of some studies addressing the importance of surface tension reduction [e.g., 2008]. The similarity between d_{act} and d_{act,HTDMA} and the small decrease in surface tension has also been suggested for aerosols over Cape Hedo, Japan, which are under the strong influence of Asian outflow [Mochida et al., 2010]. Consequently, the small lowering effect of surface tension is possibly a general characteristic of highly hygroscopic sulfate-rich particles. As suggested by 2007] and as discussed by Mochida et al. [2010], d_{act} could be lower than d_{act,HTDMA} if organics in polymeric forms absorb water and if sparingly soluble materials become more hygroscopic at high RH. Given the similarity of aerosols over the western Pacific and Cape Hedo, with their high abundance of sulfate, it is possible that the surface tension lowering effect by organics and enhancement of bulk hygroscopicity at high RH because of sparingly hygroscopic or polymeric compounds are not important under sulfate-rich conditions [Mochida et al., 2010].

3.7. Assessment of CCN Spectra Over the Western North Pacific

[28] Here, CCN spectra of aerosols observed in the MBL are estimated using d_{act} and d_{act,HTDMA} calculated using the
The activation diameter under arbitrary SS conditions, \(d_{\text{act,arb}}\), is calculated on the assumption that variables \(A\) and \(B\) in the following Köhler equation, which derive the saturation ratio \(S\) as a function of droplet diameter \(d_{\text{wet}}\), are constant.

\[
\ln S = \frac{2A}{d_{\text{wet}}} - \frac{Bd_{\text{act,arb}}^3}{d_{\text{wet}}^3 - d_{\text{act,arb}}^3};
\]

Figure 11: Plots of CCN activation diameters predicted from \(g_{\text{median}}\) \(d_{\text{act,HTDMA}}\) versus those measured \(d_{\text{act}}\). The \(d_{\text{act,HTDMA}}\) were calculated based on the core-shell model with AS, ABS, and SA as the soluble shell. They were also estimated from \(\kappa_{\text{abs}}\) based on the \(\kappa\)-Köhler theory. The solid line shows the 1:1 line. The contours with dotted lines show the expected deviation of the plots of \(d_{\text{act,HTDMA}}\) versus \(d_{\text{act}}\) from the 1:1 line as a result of changes in the surface tension (Mochida et al., 2010).

\(\kappa\)-Köhler theory. The activation diameter under arbitrary SS conditions, \(d_{\text{act,arb}}\), is calculated on the assumption that variables \(A\) and \(B\) in the following Köhler equation, which derive the saturation ratio \(S\) as a function of droplet diameter \(d_{\text{wet}}\), are constant.

\[
\ln S = \frac{2A}{d_{\text{wet}}} - \frac{Bd_{\text{act,arb}}^3}{d_{\text{wet}}^3 - d_{\text{act,arb}}^3};
\]

Based on equation (2), the critical SS \(s_c\) is expressed with \(d_{\text{act,arb}}\) as

\[
\ln(1 + s_c) = \frac{2A}{\sqrt{B}} \left( \frac{2A}{3d_{\text{act,arb}}} \right)^{\frac{1}{3}}.
\]

which can be rearranged to

\[
d_{\text{act,arb}} = \frac{2A}{3} \left( \frac{\sqrt{B} \ln(1 + s_c)}{2} \right)^{-\frac{1}{3}} = c \{ \ln(1 + s_c) \}^{-\frac{1}{3}}.
\]

Figure 12 shows \(d_{\text{act}}\) and \(d_{\text{act,HTDMA}}\) against SS and the curves fitted with equation (4). The fitted curves well represent \(d_{\text{act}}\) and \(d_{\text{act,HTDMA}}\), as estimated from \(dN_{\text{CCN}}/dN_{\text{CN}}\) and \(g_{\text{median}}\), indicating that this equation reasonably approximates the CCN activation diameters. The size range of the Hoppel minimum in Figure 12 and the comparison to the fitted curves for \(d_{\text{act}}\) and \(d_{\text{act,HTDMA}}\) suggest that the aerosols experienced cloud droplet formation on average at about 0.2%–0.3% SS. This range is similar to those estimated for southeastern Pacific aerosols from the Hoppel minimum by Tomlinson et al. (2007) (0.24 ± 0.06% and 0.20 ± 0.03% for 2003 and 2004, respectively). Furthermore, the range overlaps with that of marine stratus according to O’Dowd et al. (1997) (up to 0.3% SS).

From the curves fitted to the \(d_{\text{act}}\)-SS plots and the measured number-size distributions of aerosols, \(N_{\text{CCN}}\) versus SS were calculated for the time period studied (Figure 13a). As presented in Figure 13a, the \(N_{\text{CCN}}\) values at 0.5% and 1% SS estimated from the present study are considerably higher than those in maritime aerosols transported from southwestern and southeastern sectors to Hahajima Island in the 1990s [Nagao et al., 1999]. By contrast, the concentrations of \(N_{\text{CCN}}\) derived from the CCN spectra at 0.5% and 1% SS are more comparable to those of Hahajima aerosols under the influence of Asian continental outflow. Hudson and Noble (2009) recently reported unexpectedly high concentrations of \(N_{\text{CCN}}\) (301 cm\(^{-3}\)) at 1% SS over the mid-Pacific, in contrast to a previous report on \(N_{\text{CCN}}\) in the marine atmosphere (<200 cm\(^{-3}\)) [Twomey and Wojciechowski, 1969]. The estimated \(N_{\text{CCN}}\)...
at 1% SS in Figure 13a is also comparable to that reported by Hudson and Noble [2009]. However, the high $N_{\text{CCN}}$ presented in Figure 13a resulted from two distinctive events with high particle number concentrations in periods 1 and 3 in Figure 2b, being associated with the large increase in sulfate concentrations (Figure 5b) and with the possible influence of plumes from Kasatochi and Hawaiian volcanoes (Eguchi et al., manuscript in preparation, 2011). The mean and SD of $N_{\text{CCN}}$ derived from CCNC data are shown as solid lines and shaded gray areas, respectively, whereas those from HTDMA data are shown as dashed lines and areas between dotted lines, respectively. Mean and SD of CCN number concentrations from PASE [Hudson and Noble, 2009] are presented as the diamond and the bar. Mean CCN concentrations observed at Hahajima [Nagao et al., 1999] are presented as circles, triangles, and squares according to air mass trajectories from the northwest (continental), southwest, and southeast sectors (maritime), respectively. Mean and SD of $N_{\text{CCN}}$ derived from CCNC and HTDMA data in Figure 13a are also presented as the solid black line and the dashed red line, respectively. (d) As in Figure 13c but for period 2.
spectra in the absence of the volcanic plumes represent those of maritime aerosols in the North Pacific region. This representation in turn suggests that the concentration levels of CCN during this study were strongly perturbed by sporadic input of aerosols from other sources, resulting in the changes in particle number concentrations and hygroscopicity.

[30] Figures 13c and 13d present hypothetical CCN spectra if aerosol particles are assumed to be pure sulfate (AS, ABS, SA) or pure organics (the range of $k_{SS}$ is shown in Figure 4) without changing the number size distributions. The $N_{CCN}$ values estimated from $d_{act, arb}$ of sulfate were close to those predicted from CCNC and HTDMA data, although those estimated from $d_{act, arb}$ of organics were markedly lower, which indicates that a large abundance of sulfate sustains the level of CCN number concentrations in the studied area. Moreover, the result of the closure of $d_{act}$ in Figure 11 suggests that the large solute effect was more important than the effect of surface tension lowering because of organics for the level of $N_{CCN}$ in Figure 13. If the aerosol components were mainly of marine origin, then the result further implies a more important contribution of the DMS oxidation to $N_{CCN}$, rather than the contribution of SOA from oxidation of marine biogenic VOCs such as isoprene [Meskhidze and Nenes, 2006, 2007] and α-pinene [Yassaa et al., 2008]. Additional investigations including those for other seasons are important to improve knowledge of the relative contributions in the western Pacific MBL because the present study specifically examined a limited period and a limited type of aerosols transported mainly from the eastern to western Pacific. Further knowledge of aerosol characteristics, for example, over the northern North Pacific with high marine biological activity [Miyazaki et al., 2010] is expected to suggest avenues for additional studies.

4. Conclusions

[31] Hygroscopic growth factors and CCN activation diameters of aerosol particles in the marine boundary layer were measured simultaneously over the western North Pacific during August–September 2008. The observed aerosols were highly hygroscopic with unimodal hygroscopic growth factor distributions. They have low CCN activation diameters resembling those of sulfate aerosols. The backward air mass trajectory analysis has shown that observed aerosols mainly stagnated over the Pacific for more than 10 days, suggesting that the characteristics of remote marine air over the North Pacific were measured accurately in this study. However, particles with lower hygroscopic growth factors appeared over the northern North Pacific in accordance with the enhanced concentration of sulfate. Moreover, trajectory analysis showed that air masses measured during the event were of free tropospheric origin. The influence of the plume of Kasatochi volcano is inferred; carbonaceous (organic) aerosols transported from the free troposphere with the plume might be responsible for the observed lower hygroscopicity.

[32] The CCN activation diameters of aerosols were predicted from the median hygroscopic growth factors. The predicted activation diameters agree reasonably well with the measured activation diameters, without the assumption of the surface tension lowering effect by organics or the enhancement of bulk hygroscopicity at high RH because of sparingly soluble or polymeric compounds. This result resembles what we observed in the outflow region of sulfate-rich Asian continental aerosols (Cape Hedo, Okinawa), implying that this is the general characteristic of highly hygroscopic sulfate-rich particles. The presence of a Hoppel minimum suggests that cloud processing caused the highly hygroscopic and CCN active characteristics in the accumulation mode size range. The CCN spectra were predicted from HTDMA and CCNC data. Although the average CCN number concentrations up to >1% SS were estimated to be quite high, the concentrations excluding those at high particle concentration events, both of which might be influenced by volcanic plumes, were comparable to those described in a previous report. In other words, the results indicate that aerosol characteristics including the CCN number concentrations changed considerably with abrupt changes in air mass origins. The hypothetical CCN spectra with varying particle hygroscopicity indicate that the sulfate-rich composition sustains the concentration level of CCN over the western Pacific. Further investigations in the North Pacific region in this regard, e.g., those of the characteristics of hygroscopicity and CCN activity in the northern North Pacific area, are expected to be valuable.

[33] Acknowledgments. We thank the crew of R/V Hakuro-maru in KH-08-2 leg 2 cruise for their support of atmospheric measurements, and we thank K. Miura at Tokyo University of Science for information related to particle measurements taken during the cruise. We gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for provision of the HYSPLIT transport and dispersion model (http://www.arl.noaa.gov/ready.html). We also thank BIRA-IASB, DLR, and EUMETSAT for the use of GOME-2 images at ftp://sacs.aeronomic.be/ and we thank NASA/University of Maryland for the use of MODIS hot spot/active fire data at http://maps.geog.umd.edu. (NASA/University of Maryland is not responsible for the analysis and interpretation of the MODIS images in this study.) This study was supported by the Program for Improvement of Research Environment for Young Researchers from Special Coordination Funds for Promoting Science and Technology (SCF) commissioned by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. This study was also supported in part by Grants-in-Aid for Scientific Research 19204055 and 19030008 and the Cooperative Research Program of Ocean Research Institute, University of Tokyo. This study is a contribution to the Surface Ocean Lower Atmosphere Study (SOLAS) core project of the International Geosphere-Biosphere Programme (IGBP).

References


Pitzer, K. S., and G. Mayorga (1973), Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both


H. Furutani, J. Jung, and M. Uematsu, Atmosphere and Ocean Research Institute, University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa 277-8564, Japan.


M. Mochida and C. Nishita Hara, Institute for Advanced Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Nagoya, Japan. (mochida@iar.nagoya-u.ac.jp)