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Hygroscopic properties of particles nebulized from water extracts of aerosols collected at Chichijima Island in the western North Pacific: An outflow region of Asian dust

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[1] We present 2 year measurements of hygroscopic properties of water-soluble matter (WSM) extracted from marine aerosols from remote Chichijima Island in the western North Pacific during 2001–2002. Hygroscopic growth factors (g) of WSM were measured by a hygroscopicity tandem differential mobility analyzer with initial dry particle diameter of 100 nm. The observed g at 90% relative humidity (RH), g(90%), ranged from 1.42 to 1.89 with an average of 1.79 ± 0.11. The g values are significantly lower than that of seawater (2.1) and slightly lower than those previously reported for marine aerosols (>1.8), probably due to the atmospheric processing associated with chlorine depletion; mean Cl^-/Na^+ molar ratio (1.10 ± 0.23) was smaller than seawater (1.18), and organometal interaction (e.g., formation of water-insoluble calcium oxalate, $g(90\%) < 1$). Inorganic salts accounted for 87–98% of WSM. Na^+ and Cl^- are two major species, contributing 63% of total inorganic ion mass. The calculated aerosol water content (V_w/V_{dry}) at 85% RH during hydration experiment ranged from 1 to 3.66 (mean of 2.75 ± 0.81). V_w/V_{dry} is negatively correlated with organic mass fraction, indicating that organics may suppress the hygroscopicity of the marine aerosol particles. The declined g(90%) and Cl^-/Na^+ molar ratio and increased abundance of water-soluble organics in spring demonstrated that the atmospheric mixing of anthropogenic pollutants (e.g., NO_3, SO_x) and water-soluble organics can decrease the growth factor of marine aerosols. The two case studies of spring aerosols demonstrated that Asian dusts were internally mixed with hygroscopic species in different ways, depending on their transport pathway.

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1. Introduction

[2] The hygroscopic properties (water uptake) of atmospheric aerosols play a crucial role in determining their size and physical properties. The aerosol ability of water uptake and the subsequent growth under the conditions of increasing relative humidity (RH) lead to changes in aerosol optical properties (scattering and absorption) [*Pilinis et al*., 1995; *Randles et al*., 2004; *Khalizov et al*., 2009], visibility degradation [*Pope and Dockery*, 1999; *Jung et al*., 2009; *Liu et al*., 2012], and the Earth's radiative forcing [*Charlson et al*., 1992; *Ramanathan et al*., 2001; *Randles et al*., 2004] as well as health risks [*Dockery and Pope*, 1996]. The presence of liquid water in the atmospheric particles controls the partitioning of semivolatile species between the gas and particle phases and affects the chemical and physical properties of aerosols [*Ansari and Pandis*, 1999]. In addition, aerosol liquid water provides a medium for heterogeneous chemical reactions in the atmosphere [*Krueger et al*., 2003; *Lim et al*., 2005; *Carlton et al*., 2006].

[3] Traditionally, hygroscopic behavior of atmospheric particles has been considered to be exclusively involved with inorganic species and the hygroscopic growth of inorganic salts is much understood [*Tang*, 1976; *Chow et al*., 1994; *Saxena et al*., 1995]. In contrast, knowledge of the growth factor (GF) of the organic aerosol has been limited. Some previous studies have reported that the organic fraction in the atmospheric aerosol can alter the water content either positively [*Saxena et al*., 1995; *Gysel et al*., 2004] or negatively [*Lightstone et al*., 2000; *Choi and Chan*, 2002; *Cruz and Pandis*, 2000], depending upon the chemical composition of the aerosols. Recently, *Jung et al*. [2011] reported that water-soluble inorganic volume fraction contributed serious reduction in the mobility diameter, causing 11% underestimation in a hygroscopic growth measurement at 85% RH for organic enriched aerosols in Ulaanbaatar, Mongolia. Therefore, more information is needed to better understand the effect of organics on the liquid water content of atmospheric aerosols.

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[4] The impact of aerosol particle on the marine boundary layer is potentially high, because the ocean covers a large area of the Earth and clouds in this layer are estimated to control about one third of Earth albedo [*Charlson et al*., 1987]. Sea-salt particles that are hygroscopic deliquesce to result in aqueous solution droplets when the RH rises in the atmosphere. The chemical composition of sea-salt aerosol is complex and can vary with time and location. Reactions of sea-salt particles with sulfuric and nitric acids in the atmosphere result in a release of HCl gas, leaving the particles with reduced Cl^-/Na^+ molar ratio. Chlorine deficits in sea-salt particles may also be caused by reactions with gaseous NO_2 [*Duce et al*., 1980] or oxidation of dissolved SO_2 by O_3. Therefore, the chemical composition can be quite different between freshly produced and aged sea-salt particles. Several studies reported that organic compounds are internally mixed with sea-salt particles, constituting up to 50% of total fine aerosol mass [*Dick et al*., 2000; *Middlebrook et al*., 1998]. The organics also alter the amount of water absorbed by the aerosol particle at subsaturated RH [*Saxena et al*., 1995].

[5] Currently, the atmospheric environment of East Asia is changing due to a rapid industrialization, and thus, its outflow regions in the western North Pacific are increasingly affected by anthropogenic aerosols [*Huebert et al*., 2003]. The long-range atmospheric transport of anthropogenic aerosols from the Asian continent to the North Pacific may have significant impacts on global radiation balance, atmospheric chemistry, and marine biogeochemistry. Chichijima in the western North Pacific is a small island located on the outflow region of the Asian dusts and polluted air masses from China [*Wang et al*., 2009]. This island exists in the boundary of westerly and trade wind regimes. We have continuously collected marine aerosol samples at Chichijima Island since 1990. Previous studies have reported terrestrial lipid compound classes [*Kawamura et al*., 2003], dicarboxylic acids [*Mochida et al*., 2003], levoglucosan [*Mochida et al*., 2010], and saccharides [*Chen et al*., 2013] in aerosol samples from Chichijima; however, there is no study on the hygroscopic growth factor of the remote marine aerosols from the western North Pacific.

[6] In this study, we investigated the hygroscopic properties of the particles with initial diameter of 100 nm, which were formed by nebulization of water extracts from the Chichijima aerosols collected in 2001 to 2002 at the 5–95% RH using hygroscopicity tandem differential mobility analyzer (H-TDMA). Dynamic shape correction factor, aerosol water content, organic-inorganic interactions, and their effects on water uptake were also discussed for different seasons. Based on the results, the link between the hygroscopicity and particle chemical composition is explored.

2. Samples and Methodology

2.1. Sampling of Atmospheric Aerosols

[7] Total suspended particles (TSP) were collected on a weekly basis at the Ogasawara Downrange Station of the Japan Aerospace Exploration Agency (JAXA) in Chichijima Island (27°04′N; 142°13′E) in the western North Pacific over 4–6 days [*Chen et al*., 2013]. Aerosol particles were collected on precombusted (500°C, 3 h) quartz filters (20×25 cm, Pallflex 2500QAT-UP) using a high volume air sampler [*Kawamura et al*., 2003] with a flow rate of 1 m^3 min^{-1}. The sampler was placed at 5 m above ground level on a campus of the Satellite Tracking Center of JAXA located at the height of 254 m asl. Before the sampling, precombusted quartz filter was stored in a clean glass jar with a Teflon-lined screw cap. After the sampling, the filter was recovered into the glass jar and stored in a freezer room at −20°C prior to analysis. In this study, we used 24 samples, one sample per month (out of four or five) during the period of 2001–2002, to characterize the hygroscopicity of WSM.

2.2. Measurement of Inorganic Ions and WSOC

[8] Inorganic ions (NH_4^+, SO_4^{2-}, NO_3^-, Na^+, Cl^-, K^+, Ca^{2+}, and Mg^{2+}) were extracted from the filter samples (20 mm diameter) with organic-free ultrapure water (10 mL) (>18.2 MΩcm, Sartorius arium 611 UV) under ultra sonication. The water extracts were passed through a syringe filter (Millex-GV, 0.22 μm, Millipore) to remove the particles and filter debris, and the ions were measured using an ion chromatograph (761 Compact IC, Metrohm, Switzerland). Detailed method has been given in *Agarwal et al*. [2010]. Water-soluble organic carbon (WSOC) was extracted with organic-free ultrapure water under ultra sonication. The water extracts were subsequently passed through a syringe filter (Millex-GV, 0.22 μm, Millipore), and WSOC was measured with a carbon analyzer (Shimadzu, TOC-5000A) equipped with a catalytic oxidation column and nondispersive infrared detector [*Aggarwal and Kawamura*, 2008].

2.3. Measurement of Hygroscopic Properties

2.3.1. Hygroscopic Growth Factor

[9] The hygroscopic properties of the nebulized particles from water-soluble fraction of the filter samples were measured using H-TDMA [*Mochida and Kawamura*, 2004; *Kitamori et al*., 2009]. The principle of H-TDMA instrument is to extract narrow size cut (100 nm) of particles from polydisperse aerosols, expose them to an increased RH, and determine the diameters of the grown particles due to the water uptake at the enhanced RH. Briefly, the H-TDMA system consists of two differential mobility analyzers (DMA, TSI model 3081), an aerosol bipolar charger (Am-241), humidifiers (optional prehumidifier and aerosol humidity conditioner composed of a Nafion tube) for the aerosols and sheath flow, and a condensation particle counter (CPC, TSI model 3010). A piece of the quartz filter (7 mm diameter) was extracted with organic-free ultrapure water (7 mL) in an ultrasonic bath for 5 min (3 times). The water extracts were then filtrated with disk filters (Millex-GV, 0.22 μm, Millipore) and used for H-TDMA measurements. The aerosol particles were generated by nebulizer from WSM and were dried with two silica gel diffusion dryers down to 5% RH.

[10] The polydispersed dry aerosol particles were passed through an impactor to eliminate the super micrometer particles and a bipolar charger to prepare the singly charged particles. The charged particles were introduced into the first DMA (DMA1), where the monodispersed particles with initial diameter of 100 nm were classified. DMA1 was operated with constant flow of 0.3 and 3 LPM (Litre Per Minute) for the polydispersed aerosol and sheath air, respectively. Monodispersed dry aerosol particles were introduced to the aerosol humidity conditioner where the RH was controlled between 5% and 95%. The grown particles were then

transferred to the second DMA (DMA2), and the particle numbers were counted by a CPC. Hygroscopic growth of particles was measured with DMA2 as a function of increasing or decreasing RH between 5 and 95%. These processes are known as the hydration and dehydration experiments, respectively. A potential hysteresis can be detectable during the hygroscopic behavior of particles due to distinct phase transitions.

[11] During the hydration experiment, the RH in the flow of aerosol particles was gradually increased by controlling the dried and humidified airflows introduced to the Nafion tubing. During the dehydration experiment, the aerosol particles were prehumidified (>95%) using an optional prehumidifier before entering to humidity conditioner. The RH of the prehumidified aerosol particles was decreased gradually in the aerosol humidity conditioner. The resulting particle sizes and number concentrations were measured by DMA2 and CPC, respectively. The residence time of the particles between the aerosol humidity conditioner and DMA2 was roughly 10 s. All the H-TDMA experiments were performed at ambient temperature of 287–294 K with a mean of 291 K and atmospheric pressure (1 atm). Compressed air was used to generate the atomizer flow, dilution system flow, and sheath air flows in the H-TDMA system. The compressed air was passed through a filter (TSI Filtered Air Supply, Model no. 3074B) to remove organic particulates and through silica gel diffusion dryer to eliminate the moisture and polar VOCs.

[12] Results from the RH calibrations indicated that RH measurements for all H-TDMA studies exhibited accuracy between ±0.8% and ±1% RH and a precision of ±0.85%. In this experiment, particles (modal diameter of 100 nm) within a narrow electrical mobility band were flowed out of DMA1. The size distribution of humidified particles measured by DMA2 along with CPC also has a narrow single band with a specific width, which is originated from the classification of bandwidth of DMA1 described above as well as that of DMA2. Model diameters of the band obtained by DMA2 along with CPC were subjected to the calculation of the particle size changes [*Mochida and Kawamura*, 2004]. Size distributions of humidified particles that were corrected for diffusion losses in the H-TDMA were fitted using a lognormal Gaussian curve [*Jung et al*., 2011].

[13] The hygroscopic growth factor g(RH) of an aerosol particle can be defined as the ratio of the particle diameter at elevated RH relative to that of the initial dry particles and is given by the following equation:

$$g(\mathrm{RH}) = \frac{D(\mathrm{RH})}{D_0} \tag{1}$$

where D_0 is the initial dry particle diameter at RH < 5% and D (RH) is the diameter at an elevated RH. The analytical errors of g(RH) were ~1% at 85% RH based on the reproducibility test. This value is consistent with the previous studies using the same system [*Aggarwal et al*., 2007; *Jung et al*., 2011].

2.3.2. Shape Factor and Restructuring

[14] The hygroscopic growth factors (g(RH)) of atmospheric water-soluble matter are calculated with volume equivalent diameter (D_e), but hygroscopicity tandem differential mobility analyzer (H-TDMA) measurements are based on the mobility diameter (D_{mob}), which is only equal to the D_e for a spherical particle. The D_{mob} of a nonspherical particle can be converted into the D_e using particle dynamic shape correction factor. Because liquid droplets are always spherical, no shape correction is needed for the droplets [*Hinds*, 1999; *Krämer et al*., 2000; *Jung et al*., 2011]. Dry particles are supposed to be nearly spherical, but cracks and cavities are possibly formed in the particle structure because the particles produced by nebulizer are suddenly exposed to dry air in the diffusion dryer, leading to very fast evaporation and crystallization of the particles and resulting in a significant reduction of the mobility diameter [*Gysel et al*., 2004]. These irregularities in the dry particles can cause a discrepancy between the D_{mob} and D_e of particles. Because growth factors are referenced against the D_e, particle irregularities may bias the growth factor data.

[15] To account for restructuring, a factor is introduced that increases the measured g(RH).

$$f_n = \frac{D_e}{D_{mob}} = \frac{1}{\chi}\frac{C_c(D_e)}{C_c(D_{mob})} \tag{2}$$

where C is the Cunningham slip correction factor [*Hinds*, 1999], f_n is mobility correction factor and is defined as the ratio of minimum mobility diameter in our size spectra during the dehydration experiment to the initial mobility dry particle diameter (100 nm), χ is dynamic shape correction factor that converts between mobility and volume equivalent diameter [*Gysel et al*., 2002; *Jung et al*., 2011] and void spaces that may be present in the particle [*Ciobanu et al*., 2010]. The χ varies depending on the shape of particles. For compact spherical and cubic (sea-salt) particles, χ equals 1 and 1.08, respectively. It increases up to 2 and more for agglomerated and irregularly shaped particles [*Brockmann and Rader*, 1990].

2.3.3. Aerosol Water Content

2.3.3.1. Measured Aerosol Water Content

[16] Aerosol water content of a particle is calculated using H-TDMA data and is expressed as the water volume in a single particle (V_w) relative to the dry particle volume (V_{dry}) based on the assumption that the volumes of water and solute are additive [*Cruz and Pandis*, 2000; *Choi and Chan*, 2002; *Aggarwal et al*., 2007].

$$\text{Aerosol water content} = \frac{V_w}{V_{dry}} = \{\chi\, g(\mathrm{RH})\}^3 - 1 \tag{3}$$

where χ is a dynamic shape correction factor and g(RH) is the measured growth factor of WSM using H-TDMA.

2.3.3.2. Predicted Aerosol Water Content by Aerosol Inorganic Model

[17] The V_w/V_{dry} is predicted using an aerosol inorganic model (AIM) based on the assumption that only inorganic salts contribute to liquid water content and that organics are inert. The amount of water associated with individual inorganic salts is assumed to be additive in the prediction of V_w/V_{dry} [*Stokes and Robinson*, 1966]. The difference between RH and water activity (a_w) is ~1% due to the Kelvin effect that is considered with the surface tension of pure water.

[18] The dry particle is assumed to be composed of $(NH_4)_2SO_4$ (AS), NH_4NO_3 (AN), NH_4Cl (AC), NaCl (SC), $NaNO_3$ (SN), Na_2SO_4 (SS), and water-soluble organic matter (WSOM). In the AIM, we used molar concentrations of measured SO_4^{2-}, NO_3^-, Na^+, Cl^-, NH_4^+, and predicted H^+ to balance the charge.

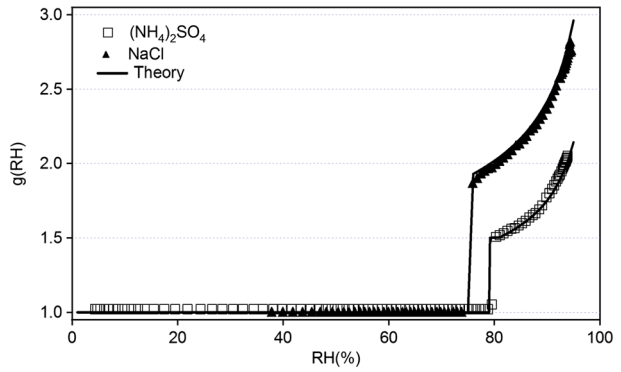


Figure 1. Measured hydration curves for $(NH_4)_2SO_4$ and NaCl. Solid lines represent theoretical prediction using AIM. The g(RH) of NaCl below 35% RH was removed due to the restructuring of particles during the hydration measurement. Initial dry particle diameter is 100 nm.

[19] The mass of water content (m_w^{ext}) associated with the inorganic species at varying RH (a_w) is calculated using the AIM as

$$m_w^{ext} = f_{AIM}\left(m_{AS}^{ext}, m_{AN}^{ext}, m_{AC}^{ext}, m_{SS}^{ext}, m_{SC}^{ext}, m_{SN}^{ext}\right) \quad (4)$$

where m_{AS}^{ext}, m_{AN}^{ext}, m_{AC}^{ext}, m_{SS}^{ext}, m_{SC}^{ext}, and m_{SN}^{ext} are the masses of AS, AN, AC, SS, SC, and SN in a unit volume of water extracts, respectively.

[20] Therefore, for an ideal case, the V_w/V_{dry} ratio is predicted by AIM model as

$$\text{Predicted AWC} = \left(\frac{V_w}{V_{dry}}\right)_{AIM} = \frac{\left(\frac{m_w^{ext}}{\rho_w}\right)}{\left(\frac{m_{AS}^{ext}}{\rho_{AS}} + \frac{m_{AN}^{ext}}{\rho_{AN}} + \frac{m_{AC}^{ext}}{\rho_{AC}} + \frac{m_{SS}^{ext}}{\rho_{SS}} + \frac{m_{SC}^{ext}}{\rho_{SC}} + \frac{m_{SN}^{ext}}{\rho_{SN}} + \frac{m_{WSOM}^{ext}}{\rho_{WSOM}}\right)} \quad (5)$$

where ρ is the density and m_{WSOM}^{ext} is the mass concentration of WSOM (WSOC×2.1, as suggested by *Aggarwal et al.* [2007]) in a unit volume of the water extracts.

2.3.4. ZSR Mixing Rule

[21] The hygroscopic growth factor of mixture can be estimated from the growth factors of individual components of the aerosol and their respective volume fraction (ε) with the ZSR (Zdanovskii-Stokes-Robinson) relation [*Stokes and Robinson*, 1966] as

$$g_{mixed}(RH) = \left(\sum_i \varepsilon_i g_i(RH)^3\right)^{1/3} \quad (6)$$

where g_{mixed} is the growth factor of the mixed particles, g_i(RH) is the growth factor of individual component, and ε_i is its respective volume fraction. The model assumes as follows: The particles are spherical, mixing behavior is ideal, and water uptake of the organic and inorganic components is independent.

2.3.5. Changes in Water Content Due to Organics (ξ_w)

[22] In order to evaluate the effect of the organic fraction on the hygroscopic growth of inorganic fraction, the hygroscopic growth of the particle due to inorganic species was compared to that of the total growth by a mixed particle [*Cruz and Pandis*, 2000]. The change in water content due to organics (ξ_w) is calculated as

$$\xi_w = \frac{\text{Water volume uptake by the mixed particle}}{\text{Water volume uptake by the inorganic fraction}} = \frac{(GF)^3 - 1}{(1-\varepsilon_0)\left((GF)^3_{INORG} - 1\right)} \quad (7)$$

where GF is the measured g(RH) for the laboratory-generated WSM particle, ε_0 is the volume fraction of organics ($1-\varepsilon_{soluble}$), and GF_{INORG} is the growth factor for the inorganic component at the relative humidity of interest calculated by the AIM [*Clegg et al.*, 1998]. The ξ_w corresponds to the error incurred by assuming that the inorganic fraction of the particle only interacts with water and organics behave like an inert material.

2.3.6. Non-Sea-Salt Calcium Concentration

[23] In order to investigate the continental dust influence, non-sea-salt calcium (nss Ca^{2+}) concentrations are calculated using the following equation by assuming that the chemical composition of sea-salt particles are the same as those of sea water and Na^+ in particulate samples originated solely from sea salt [*Park et al.*, 2004].

$$\text{nss } Ca^{2+}\ (\mu g\ m^{-3}) = \left[Ca^{2+}(\mu g\ m^{-3})\right] - \left[Na^{+}(\mu g\ m^{-3})\right] \times 0.0373 \quad (8)$$

3. Results and Discussion

3.1. Validation of H-TDMA Using Chemical Standards

[24] The g(RH) of pure salts generated from aqueous solution were measured to validate proper H-TDMA sizing and operation. The measured g(RH) curves of $(NH_4)_2SO_4$ and NaCl salts with an initial dry particle diameter of $D_0 = 100$ nm during hydration experiment is shown in Figure 1. The solid line designates a predicted growth factor based on the AIM [*Clegg et al.*, 1998], considering Kelvin effect with a density of 1.76 g cm^{-3} for $(NH_4)_2SO_4$ and 2.16 g cm^{-3} for NaCl and with dynamic shape correction factor (χ) of 1.02 for $(NH_4)_2SO_4$ [*Biskos et al.*, 2006; *Zelenyuk et al.*, 2006; *Suda and Petters*, 2013] and 1.08 for NaCl [*Krämer et al.*, 2000; *Gysel et al.*, 2002]. The g(85%) of $(NH_4)_2SO_4$ was 1.57 ± 0.01 ($n = 3$) and that of NaCl was 2.17 ± 0.02 ($n = 3$), which are in good agreement with theoretical growth factors calculated by the AIM, i.e., g(85%) = 1.56 for $(NH_4)_2SO_4$ and 2.16 for NaCl.

3.2. Hygroscopic Growth Factors of Aerosol WSM

[25] The hygroscopic growth factor, g(RH), was calculated by choosing a minimum mobility diameter (D_{min}) during the dehydration experiment [*Gysel et al.*, 2004; *Jung et al.*, 2011]. Figure 2 shows averaged g(RH) of WSM samples ($n = 24$) as a function of RH during the hydration and dehydration experiments. The measured g(RH) at high RH (>80%) are very similar between two experiments. The mean g(RH) of WSM was 1.54 ± 0.12 at 85% RH and 1.76 ± 0.11 at 90% RH during the hydration experiment. The g(RH) of the dehydration experiment is higher than that of the hydration experiment at lower RH (30–80%) (Figure 2), probably due to a hysteresis effect. The hysteresis phenomenon was observed for most of the samples from

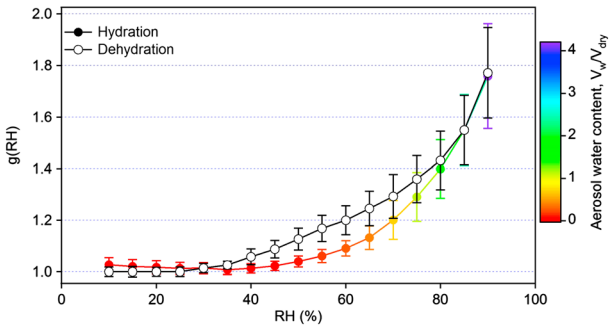


Figure 2. Changes in average growth factors, g(RH), as a function of RH on hydration and dehydration modes. The g (RH) from 5% to 90% RH with 5% increments were calculated for each sample by interpolation at the nearest RH and then were averaged. Also, changes in aerosol water content, V_w/V_{dry}, are measured by H-TDMA on hydration mode as a function of RH. The vertical bar passing through the points denoted by $\pm\sigma$ standard deviation.

Chichijima. However, there was a slight overestimation of g (RH) (1.05) on the hydration mode at lower RH (<50%). It is mainly due to the reduction in the mobility diameter at 20–50% RH, which is also called as a microstructural rearrangement and can be explained by the nonspherical shape of the laboratory-generated WSM (nebulized from water extracts, see section 2.3.2). The dynamic shape factors for the laboratory-generated WSM particles in this study ranged from 1.02 to 1.11 with a mean value of 1.07 ± 0.03 (Table 1). This calculated mean χ value is very close to that (1.08) of the cubic particles of NaCl. This fact may indicate that the g(RH) of the WSM particles from Chichijima is mainly due to the sea salt, which is probably the most important hygroscopic component.

[26] Figure 3 presents RH dependences of the g(RH) and V_w/V_{dry} during the hydration and dehydration experiments for the sample collected during 24–29 January 2001. As the RH increases, the WSM particle stays as solid until the RH reaches the deliquescence RH (DRH) for one of the salts in the WSM particles during the hydration experiment. At this DRH the substance starts to absorb water vapor and reaches the saturated aqueous solution. The aqueous solution causes the partial dissolution of remaining salt species, with their partitioning between solid and liquid phases being governed by the thermodynamic equilibrium. As the RH further increases, the second salt in the WSM particles deliquesces to obtain additional water. A similar process is repeated until all the salts are dissolved. As the RH decreases during the dehydration experiment, the growth factor decreases due to the evaporation of water. However, some species in the aqueous solution of WSM does not crystallize at DRH but remains supersaturated until very low RH is achieved. Similar studies have been made to determine the behavior of particles nebulized from water extracts of aerosol as a function of RH [*Ho et al.*, 1974; *Dzubay et al.*, 1982; *Gysel et al.*, 2004; *Aggarwal et al.*, 2007; *Jung et al.*, 2011; *Kristensen et al.*, 2012].

3.3. Aerosol Water Content in Aerosol WSM

[27] The aerosol water content plays an important role in controlling the size and composition of the atmospheric particles and influencing the total particulate mass and its optical properties. The measured aerosol water content (V_w/V_{dry}) varied from 1.00 to 3.66 with a mean of 2.75 ± 0.81 at 85% RH during hydration experiment (Figure 2). This mean V_w/V_{dry} value is compared to the values predicted from the AIM model. We found that the H-TDMA derived V_w/V_{dry} are significantly lower than the model predicted V_w/V_{dry}. This perturbation is mainly caused by the presence of water-soluble organics in WSM. This result also signifies that the observed underestimation of aerosol water content based on H-TDMA could be due to a reduced hygroscopic growth rate of the particles, which may be caused by the presence of organics or organic-inorganic interactions in the extracted WSM. These interactions can be positive and negative, depending on the organic mass fraction and type of salt [*Cruz and Pandis*, 2000]. This result again suggests that organics in aerosols likely cause a negative effect on hygroscopicity of the atmospheric particles at Chichijima. This point is further supported by the following results.

[28] The changes in water content due to organics (ξ_w) can be used to determine whether the effect of organics on total water uptake has positive or negative. If $\xi_w > 1$, organics in the particles enhance the absorption of water either by increasing the hygroscopic growth of the inorganic fraction or absorbing water by itself. If $\xi_w < 1$, organics suppress the hygroscopic growth of the particles and thus decrease the total water uptake. A value of $\xi_w = 1$ indicates that organics are inert and do not have any effect on the water uptake capability of particles. The calculated ξ_w values ranged from 0.39 to 0.78 (see Figure 4) with a mean value of 0.52 ± 0.11 at 85% RH during the 2 year study period at Chichijima. The ξ_w values of less than 1 for all the Chichijima WSM samples indicate that the presence of organics depresses the hygroscopic growth of particles (negative effect).

[29] *Saxena et al.* [1995] reported that the organic fraction enhances the water uptake of inorganic aerosol particles in nonurban locations but diminishes in urban environments.

Table 1. Mobility Correction Factor (f_n) and Dynamic Shape Correction Factor (χ) of Particles Nebulized From Water Extracts of Chichijima Aerosols During 2001–2002

Sample ID	Mobility Correction Factor (f_n)	Dynamic Shape Correction Factor (χ)
24–29 January 2001	0.98	1.04
19–25 February 2001	0.98	1.04
5–9 March 2001	0.99	1.02
16–20 April 2001	0.98	1.04
7–11 May 2001	0.98	1.04
4–8 June 2001	0.98	1.04
2–6 July 2001	0.98	1.04
6–10 August 2001	0.95	1.09
17–21 September 2001	0.95	1.09
15–19 October 2001	0.95	1.09
5–9 November 2001	0.94	1.11
10–14 December 2001	0.95	1.09
21–25 January 2002	0.95	1.09
18–22 February 2002	0.96	1.07
18–22 March 2002	0.96	1.07
15–19 April 2002	0.96	1.07
20–24 May 2002	0.95	1.09
17–21 June 2002	0.95	1.09
15–19 July 2002	0.95	1.09
19–23 August 2002	0.95	1.09
24–27 September 2002	0.96	1.07
21–24 October 2002	0.95	1.09
18–22 November 2002	0.94	1.11
16–20 December 2002	0.96	1.07

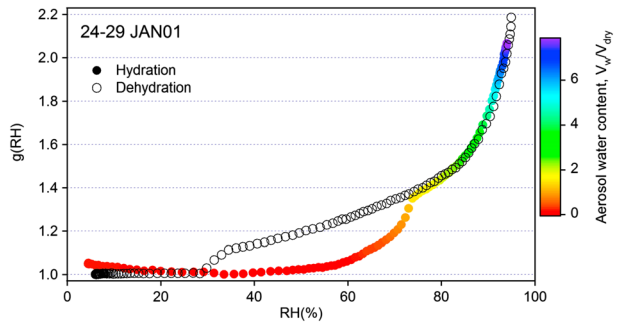


Figure 3. An example of RH dependence of hygroscopic growth factor (g(RH)) of Chichijima aerosol sample 24–29 January 2001 during hydration and dehydration measurements. Aerosol water content (V_w/V_{dry}) during hydration is also shown in color scale.

Cruz and Pandis [2000] found that ξ_w values at g(85%) for the systems of NaCl-glutaric acid (1:1 M ratio) and $(NH_4)_2SO_4$-glutaric acid (1:1 M ratio) ranged from 0.5 to 0.8 and 1.2 to 1.4, respectively. Also, they reported that at low organic mass fraction (<50%), the water uptake by the NaCl is reduced by 30%. While at organic mass fraction >50%, the water uptake by the particles is reduced by as much as 20%. *Dick et al*. [2000] found that organic-associated water content is less than that of sulfate compounds at high RH but comparable at low RH. Therefore, it is very likely that the interaction of organic-inorganic species can decrease the growth factor of the remote marine aerosols, which may be associated with the presence of WSOC. This is possibly caused by the formation of oxalate-metal complex that is not water soluble [*Furukawa and Takahashi*, 2011]. These points will be discussed with more details in section 3.4.1.

[30] Figure 5 presents relations between the aerosol water content (V_w/V_{dry}) measured by H-TDMA and organic mass fraction to further examine the role of organics on the aerosol water content. We clearly found that V_w/V_{dry} ratios decrease with an increase in the organic mass fraction with the correlation coefficient (R^2) of 0.64. It is also worthwhile to note that aerosol water content was to some extent controlled by organic species even though it has minor contribution in Chichijima marine aerosol (TSP) samples collected for 2001–2002. However, size-segregated samples may provide totally different pictures on hygroscopic properties depending on particle sizes, in which chemical compositions are very variable.

3.4. Temporal and Seasonal Variations of Chemical Species and Hygroscopic Growth Factor

3.4.1. Cl^-/Na^+ Molar Ratio Versus Hygroscopic Growth Factors of Aerosol WSM Particles

[31] Figure 6 shows temporal variations of chemical species, Cl^-/Na^+ molar ratio, and g(RH) for the aerosol filter samples. Chemical data of ions showed that the inorganic salts accounted for 87–98% of the water-soluble masses (inorganic ions plus WSOM) and the remaining fraction was water-soluble organic matter (WSOM). Chloride and sodium are found as dominant species (see Figure 6a), which contribute 63% of total inorganic mass, followed by sulfate. Concentrations of SO_4^{2-} were highest (8.5 μg m^{-3}) on 18–22 March 2002 and lowest (0.31 μg m^{-3}) on 07–11 May 2001, whereas those of NO_3^- were highest (3.63 μg m^{-3}) on 18–22 March 2002 and lowest (0.07 μg m^{-3}) on 20–24 May 2002. NH_4^+ concentrations were generally low throughout the sampling period although high value was recorded on 18–22 March 2002. The mean Cl^-/Na^+ molar ratios were found to be highest (1.34) on 17–21 September 2001 and lowest (0.30) on 20–24 May 2002 with a mean value of 1.10 ± 0.23, which is lower than that of bulk seawater (1.18). This result suggests that chlorine loss occurs to some extent in the marine aerosols during transport.

[32] Acid displacement or atmospheric processing is probably responsible for the chloride depletion. Although t test showed that the overall difference between the Cl^-/Na^+ ratio and seawater molar ratio is not statistically significant (p = 0.14), the difference in a case study (see section 3.4.2) is statistically significant (p = 0.003). Concentrations of WSOC ranged from 0.11 μg m^{-3} to 0.90 μg m^{-3} with a mean of 0.36 ± 0.21 μg m^{-3}, showing highest value (0.90 μg m^{-3}) on 18–22 March 2002 and lowest value (0.11 μg m^{-3}) on 20–24 November 2002. The measured hygroscopic growth factor g(RH = 85 and 90%) was highest (1.67 and 1.89) on 15–19 July 2002 and lowest (1.23 and 1.42) on 20–24 March 2002 with a mean of 1.54 ± 0.12 and 1.79 ± 0.11, respectively (Figure 6b and Table 2).

[33] Figure 7 presents seasonally averaged concentrations of chemical species, Cl^-/Na^+ molar ratios, and g(RH). Sea spray components such as Na^+ and Cl^- maximized in winter followed by spring and autumn and minimized in summer. SO_4^{2-}, NO_3^-, NH_4^+, and Ca^{2+} maximized in spring followed by winter (see Figure 7a), probably due to the influence of the outflow of Asian dusts. The concentrations of nss Ca^{2+} in TSP samples drastically increased in spring when the Asian dusts were transported over the western North Pacific by westerly winds. This result is consistent with the observation at Gosan site, Jeju Island in the East China Sea, where Ca^{2+} concentrations maximized in spring although its concentrations are much higher at Gosan site [*Kawamura et al*., 2003]. *Guo et al*. [2011] also reported that concentrations of nss Ca^{2+} in PM_{10} significantly increased when the Asian dust storm invaded in Monzenmachi, Japan. Similar results were observed at Mt. Fuji [*Suzuki et al*., 2008]. WSOC in the Chichijima aerosols maximized in spring and minimized in summer. The Cl^-/Na^+ molar ratios are lower in spring and higher in autumn

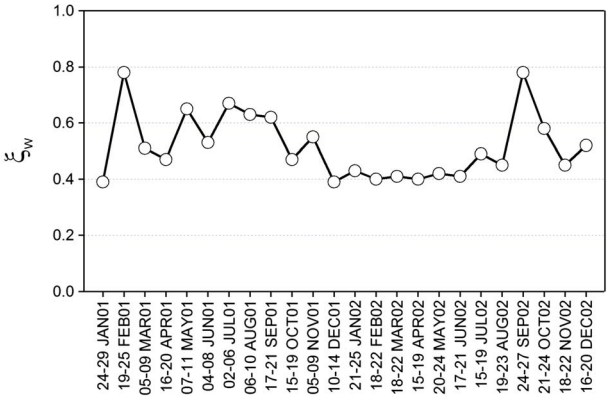


Figure 4. Variation of change in water content, ξ_w, during the sampling period at Chichijima.

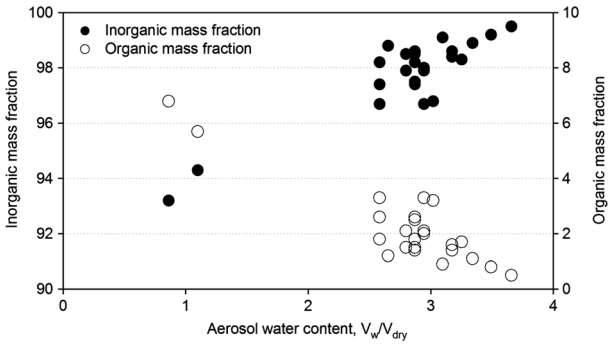


Figure 5. Relationship between the measured aerosol water content and organic and inorganic mass fractions in the aerosol samples from Chichijima Island.

and winter followed by summer. Interestingly, the measured g (85%) values declined in spring. In contrast, enhanced g(85%) was observed in autumn and winter. Similar trends were obtained for g(90%) (see Figure 7b).

[34] The declined g(85%) during spring is likely due to the chemical aging of dust particles probably via forming calcium sulfate and calcium oxalate monohydrate, which are less hygroscopic (hygroscopicity parameter, kappa $\kappa = 0.005$) and less cloud condensation nuclei (CCN) active [*Sullivan et al.*, 2009]. In fact, calcium oxalate monohydrate is less hygroscopic than oxalic acid ($\kappa = 0.3$) [*Prenni et al.*, 2001]. *Mochida et al.* [2003] have reported high abundance of oxalic acid in the Chichijima aerosols in spring. Oxalic acid may be internally mixed with dust-derived minerals. This mixing state could reduce the water solubility of oxalic acid and thus reduce its hygroscopicity. Pure oxalic acid does not deliquesce in the range of 10–90% RH [*Peng et al.*, 2001]. Previous studies of Asian dust showed that oxalate was largely mixed with mineral dust particles during atmospheric transport [*Sullivan and Prather*, 2007]. *Furukawa and Takahashi* [2011] detected calcium oxalate in spring dusts over Tsukuba, Japan using X-ray absorption fine structure spectroscopy. Recently, *Ma and He* [2012] reported that a synergistic effect plays an important role on the humidification process of calcite, calcium nitrate, and oxalic acid mixtures. The formation of calcium oxalate through the synergistic process can decrease the hygroscopic property of mixed particles.

[35] In contrast, *Kim and Park* [2012] reported that Asian mineral dusts collected at Gwangju, Korea, had interacted with anthropogenic pollutants during long-range transport, leading to the formation of secondary sulfate and nitrate and the increase in the hygroscopicity of the sampled aerosols.

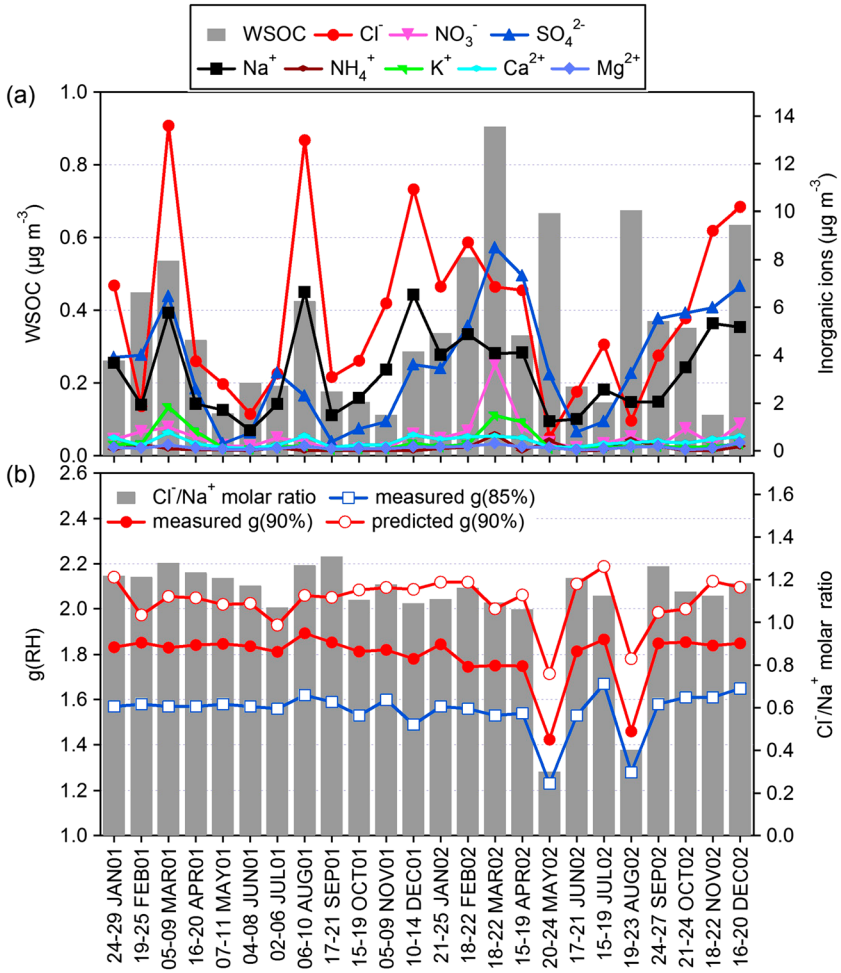


Figure 6. Temporal variation of (a) water-soluble ions and (b) Cl^-/Na^+ molar ratio, g(RH) at 85% and 90% RH during 2001–2002 period at Chichijima.

Table 2. Measured and Predicted g(90%) of Chichijima Aerosols During 2001–2002

Sample ID	Growth Factor at 90% RH, g(90%)		Uncertainty in g(90%) (%)
	Measured	Predicted	
24–29 January 2001	1.83	2.14	14
19–25 February 2001	1.85	1.87	1
5–9 March 2001	1.83	2.05	11
16–20 April 2001	1.84	2.05	10
7–11 May 2001	1.85	2.02	8
4–8 June 2001	1.84	2.02	9
2–6 July 2001	1.81	1.93	6
6–10 August 2001	1.89	2.06	8
17–21 September 2001	1.85	2.05	10
15–19 October 2001	1.81	2.08	13
5–9 November 2001	1.82	2.09	13
10–14 December 2001	1.78	2.09	15
21–25 January 2002	1.84	2.12	13
18–22 February 2002	1.75	2.12	17
18–22 March 2002	1.75	2.00	13
15–19 April 2002	1.75	2.06	15
20–24 May 2002	1.42	1.71	17
17–21 June 2002	1.81	2.11	14
15–19 July 2002	1.87	2.19	15
19–23 August 2002	1.46	1.78	18
24–27 September 2002	1.85	1.91	3
21–24 October 2002	1.85	2.00	8
18–22 November 2002	1.84	2.12	13
16–20 December 2002	1.85	2.10	12
Average	1.79	2.02	11

However, it is not true in the case of mixed oxalic acid and calcite since the hygroscopicity and CCN activity of calcium oxalate are similar to calcite and less than those of oxalic acid [*Sullivan et al.*, 2009]. Moreover, the hygroscopicity of calcium nitrate will also be lowered by mixing with oxalic acid [*Ma and He*, 2012]. Therefore, the formation of less hygroscopic calcium oxalate plays a significant role in aged mineral dust particles, resulting in the decrease of hygroscopicity of the particles.

[36] On the other hand, the loss of chlorine from mineral dust particles in the marine boundary layer due to the heterogeneous reactions on aerosols [*Sullivan et al.*, 2007] may decrease the Cl^-/Na^+ molar ratio, lowering the g(85%) values. Because marine aerosols are largely comprised of water-soluble inorganic components, the measured growth factor at RH = 90% for marine aerosols can be directly considered to be hygroscopic [*Mochida et al.*, 2010, 2011]. However, we found that the measured growth factors are significantly lower than that of seawater as stated above. *Nilsson* [2007] reported that H-TDMA growth factors measured for seawater samples taken from the Baltic Sea (water depth, 1–2 m) and Atlantic (~3000 m) to be g(90%) = 2.1 for 100 nm dry size particles, which is in good agreement with the seawater-water activity reported by *Tang et al.* [1997] with Electrodynamic Balance. Interestingly, the observed mean growth factor g(90%) = 1.79 at Chichijima is slightly lower than those (g(90%) > 1.85) reported for the marine aerosols from different sites [*Sverdrup et al.*, 1942;

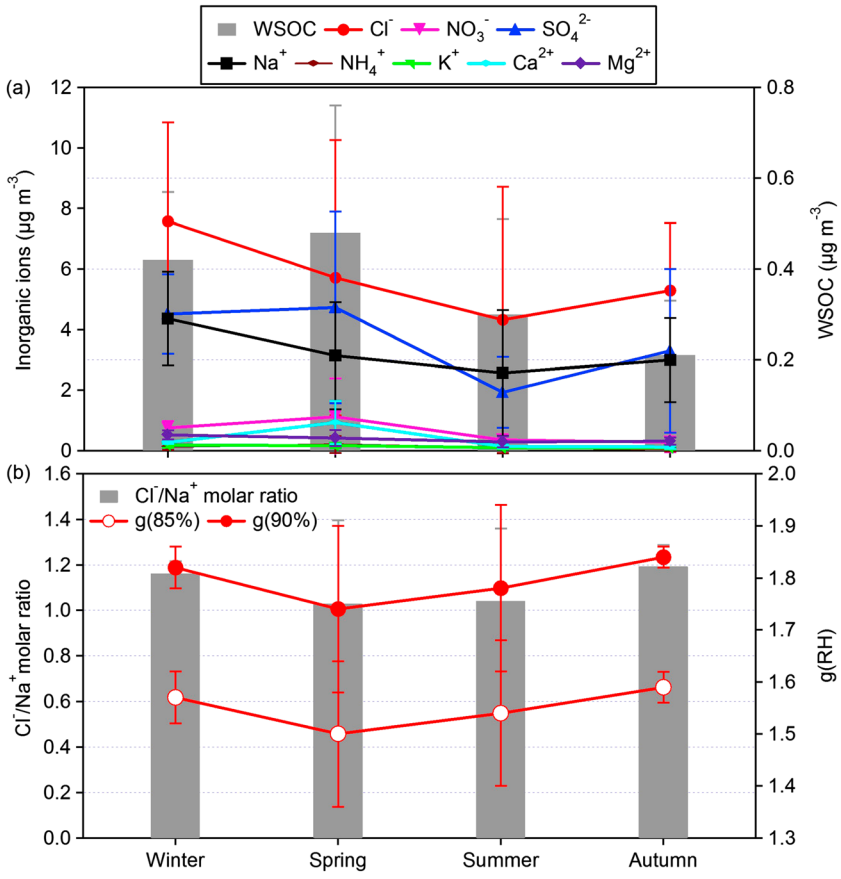


Figure 7. Seasonal variations of (a) water-soluble ions and WSOC and (b) Cl^-/Na^+ molar ratio and g (RH) at 85% and 90% RH during 2001–2002 period at Chichijima.

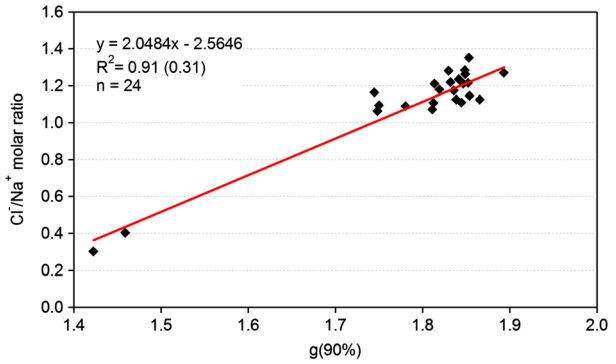


Figure 8. Correlation plot between $g(90\%)$ and Cl^-/Na^+ molar ratio.

Fabuss et al., 1966; *Tang*, 1997; *Nilsson*, 2007; *Swietlicki et al*., 2008].

[37] Based on the chemical composition data, we consider that the reduction of the $g(90\%)$ of Chichijima aerosols is probably due to the formation of sodium sulfate/sodium nitrate as a result of chlorine loss reaction. These particles have smaller growth factors than NaCl [*Randles et al*., 2004; *Modini et al*., 2010]. *Berg et al*. [1998] and *Swietlicki et al*. [2000] reported that atmospheric processing of freshly produced sea-salt particles results in mixtures consisting primarily of sodium, chloride, sulfate, and ammonium ions and organic compounds from gas phase deposition, causing a gradual decrease in $g(90\%)$ during Aerosol Characterization Experiment ACE-1and ACE-2. *Kerminen et al*. [1998] also found that the main constituents replacing chloride from sea-salt particles were sulfate and nitrate followed by methanesulfonate and oxalate, while malonate and succinate gave a minor contribution. Therefore, it is possible that substitution of chloride by oxalic acid and conversion of oxalic acid to disodium oxalate results in a decrease in the hygroscopicity of Chichijima aerosols. Recently, *Ma et al*. [2013] found that due to the high contribution of oxalic acid to organic aerosols, acid displacement reactions between oxalic acid and sea salts may play a significant role in the hygroscopicity change. The declined $g(90\%)$ and Cl^-/Na^+ molar ratio and increased concentrations of WSOC in spring demonstrate that the atmospheric processing of pollutants and water-soluble organic aerosols can diminish the hygroscopicity of mixed particles.

[38] The above point is further supported by a strong correlation ($R^2 = 0.91$) between the Cl^-/Na^+ molar ratio and $g(90\%)$ as shown in Figure 8. This positive correlation indicates that hygroscopic growth is mainly controlled by the sea-salt (NaCl) particles. It is of interest to note that in the samples 20–24 May 2002 and 19–23 August 2002, a drastic reduction of $g(90\%)$ was observed with very low Cl^-/Na^+ molar ratios. However, the Cl^-/Na^+ ratios still positively correlate with $g(90\%)$ with a correlation coefficient of $R^2 = 0.31$ when the two samples (20–24 May 2002 and 19–23 August 2002) are excluded (Figure 8). This result suggests that chemical aging associated with Cl loss generally suppresses the hygroscopic growth of marine aerosols in the western North Pacific, an outflow region of Asian continental pollutants.

[39] Furthermore, we have calculated theoretically predicted growth factors using ZSR mixing model over the observation site (see Figure 6b). The results showed that the predicted growth factors are higher on average by 11% than the measured growth factors at 90% RH using H-TDMA (Table 2). These results are consistent with previous measurements [*Ming and Russell*, 2001; *Quinn et al*., 2004; *Kaku et al*., 2006; *Svenningsson et al*., 2006; *Modini et al*., 2010]. *Kaku et al*. [2006] reported that the predicted growth factor for the aerosol particles over the northeastern Pacific is overestimated by more than 30% (on average). *Ming and Russell* [2001] studied the predicted growth factors for sea-salt particles using explicit thermodynamic calculation [*Ming and Russell*, 2002] for various mixed organic-inorganic systems. They showed that if aerosol particles have 30% and 50% of organic mass, the reductions of growth factor above 75% RH are 15% and 25% lower than those of the ZSR model, respectively. Such a discrepancy is probably caused by the presence of marine organic compounds or interaction between inorganic and anthropogenic organic species in aqueous solution [*Ming and Russell*, 2001]. This discrepancy also suggests an important uncertainty in the global aerosol radiative effect [*Adams et al*., 1999]. *Quinn et al*. [2004] also reported that for Asian Pacific aerosols (ACE-Asia) using the same thermodynamic model, the predicted water uptake is insensitive to the assumptions about the water solubility of the organic species. Therefore, the ZSR model may not provide a good approximation for the processed sea-salt aerosols.

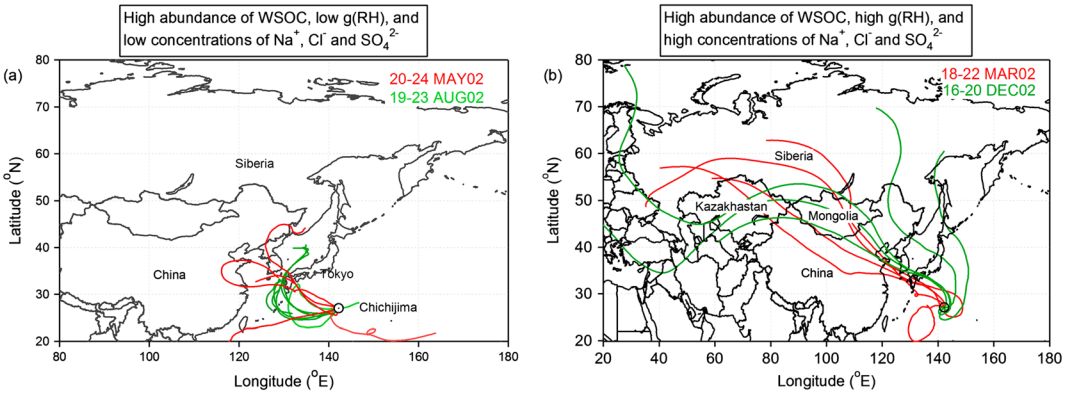


Figure 9. Seven-day backward trajectories of air masses that arrived at Chichijima (a) during 20–24 May 2002 and 19–23 August 2002 and (b) 18–22 March 2002 and 16–20 December 2002. The trajectories were calculated every 24 h [*Draxler and Rolph*, 2003].

3.4.2. Two Case Studies

[40] To better understand chemical aging of Asian dust particles during long-range atmospheric transport, we examined two types of samples. The first type (Type I) of samples is characterized by high abundance of WSOC, low g(RH), and low concentrations of Na^+, Cl^-, and SO_4^{2-}, which includes two samples of 20–24 May 2002 and 19–23 August 2002. The second type (Type II) is characterized by high abundance of WSOC, high g(RH), and high concentrations of Na^+, Cl^-, and SO_4^{2-}, which includes two samples of 18–22 March 2002 and 16–20 December 2002. Air mass trajectories have been used to search the source region of air mass over the observation site. Figure 9 represents 7 day back trajectories for the Chichijima aerosol samples. Based on the air mass trajectories and meteorological parameters, we deeply analyzed the differences in g(RH) as follows. Generally, the air masses came from inland China, Siberia, Korea, and Japan during winter and spring, whereas pristine oceanic air masses came from the Pacific Ocean to the Chichijima site in summer and autumn [*Chen et al*., 2013]. Interestingly, Type I samples (20–24 May 2002 and 19–23 August 2002) were collected when air masses were transported from eastern China, Korea, and southern parts of Japan over the sampling site (Figure 9a). The air mass trajectories are quite opposite to the general seasonal pattern of trajectories for these months. It is also important to note that these air masses carried abundant WSOC with lower contents of Na^+, Cl^-, and SO_4^{2-} (see Figure 6a), showing lower growth factors during the sampling periods (see Figure 6b).

[41] The air masses for Type II samples originated from Arabian countries picking up mineral dusts and traveled long distances passing over Siberia, Mongolia, China, Korea, and Japan before arriving at Chichijima (see Figure 9b). Although the highest concentration of WSOC was recorded in Type II event (18–22 March 2002 sample), we detected a decreased growth factor for the samples of 20–24 May 2002 and 19–23 August 2002 (Figure 6b). These results suggest that WSOC components significantly suppress the hygroscopicity of marine aerosols. Moreover, Figure 6 reveals that when Cl^-/Na^+ molar ratios decrease, concentrations of WSOC increase, indicating that more anthropogenic inputs from the Asian continent (see Figure 9a) or more aged continental air mass had arrived over the sampling site during Type I than Type II event. Although hygroscopicity of marine aerosols in the western North Pacific is mainly controlled by sea salts, long-range atmospheric transport of anthropogenic WSOC can negatively alter their hygroscopic properties. Atmospheric chemical processing (aging) significantly alters the original dust composition, leading to the changes in the physicochemical properties of transported Asian dust particles. The mode of aging in the atmosphere may be different, depending on the air mass pathways, which again provide different chemical constituents of aerosols [*Tobo et al*., 2010].

4. Summary and Conclusions

[42] In this study we investigated hygroscopic properties of the particles nebulized from water-soluble materials (WSM) extracted from marine aerosol samples (TSP) that were collected over a remote marine site (Chichijima) in the western North Pacific during the 2001–2002 period using H-TDMA with an initial dry particle diameter (D_0) of 100 nm.

[43] The measured hygroscopic growth factors g(90%) ranged from 1.42 to 1.89 with a mean value of 1.79 ± 0.11. These values are significantly lower than that of seawater (2.1) and slightly lower than those previously reported for marine aerosol growth factors (>1.8), probably due to the chlorine deficits in sea-salt particles (atmospheric processing) and organometal interaction (formation of calcium oxalate) during long-range atmospheric transport. The calculated Cl^-/Na^+ molar ratios varied in a range of 0.30–1.34 with a mean of 1.10 ± 0.23, which is lower than that of seawater (1.18).

[44] The observed mean growth factor and aerosol water content (V_w/V_{dry}) at 85% RH during hydration experiment were 1.54 ± 0.12 and 2.75 ± 0.81, respectively. The g(85%) are negatively correlated with organic mass fractions, indicating that organics may suppress the hygroscopicity of the marine aerosol particles. The change in aerosol water content (ξ_w) was less than 1 for all the WSM samples from Chichijima, indicating that aerosol water volume decreased by the presence of organics.

[45] The declined g(90%) and Cl^-/Na^+ molar ratio and high abundance of WSOC in spring demonstrated that the atmospheric mixing of anthropogenic pollutants (e.g., NO_3, SO_x) and water-soluble organics can decrease the growth factor of the marine aerosol particles. A strong positive correlation was observed between g(90%) and Cl^-/Na^+ molar ratio, indicating that reduction of growth factor is linked to the chemical aging during long-range atmospheric transport via the interaction with anthropogenic pollutants. Further, the ZSR model shows that the discrepancy (11%) is present between measured and predicted growth factors, probably due to the interaction of organics with sea-salt species during the atmospheric transport. The case study of spring aerosols explained that Asian dusts were internally mixed with hygroscopic species in different ways depending on their transport pathway.

[46] We demonstrate that the hygroscopicity of remote marine aerosols (TSP) from the western North Pacific is mainly caused by the sea-salt components and the contribution of organic matter is rather small. However, when aerosols are enriched with water-soluble organic materials, the hygroscopicity of the particles decreases. Based on the 2 year observation, we conclude that atmospheric aging associated with chlorine deficits in sea-salt particles and interactions of water-soluble organics with dust particles often suppress the water uptake properties of the particles in the outflow region of Asian dust.

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