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Hygroscopic growth of water-soluble matter extracted from remote marine aerosols over the western North Pacific: Influence of pollutants transported from East Asia

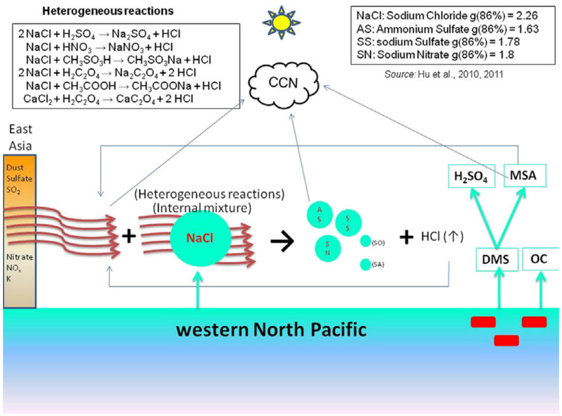
S.K.R. Boreddy, K. Kawamura *

Institute of Low Temperature Science, Hokkaido University, N19, W8, Kita-ku, Sapporo 060-0819, Japan

HIGHLIGHTS

- Hygroscopic properties of water-soluble matter were investigated using HTDMA.
- Growth factors of 100 nm dry particles were measured in the range of 5–95% RH.
- $g(90\%)$ was significantly controlled by sea salts over the western NP.
- Long-range transported pollutants and dust could suppress the $g(90\%)$.
- HCl liberation leads to the less hygroscopic aerosol particles.

GRAPHICAL ABSTRACT



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ABSTRACT

We examined the hygroscopic properties of water-soluble matter (WSM) nebulized from water extracts of total suspended particles (TSP) collected at Chichijima Island in the western North Pacific during January to September 2003. The hygroscopic growth factor $g(\mathrm{RH})$ of the aerosol particles was measured using a hygroscopic tandem differential mobility analyzer (HTDMA) with an initial dry particle diameter of 100 nm and relative humidity (RH) of 5–95%. The measured growth factor at 90% RH, $g(90\%)$, ranged from 1.51 to 2.14 (mean: 1.76 ± 0.15), significantly lower than that of sea salts (2.1), probably owing to the heterogeneous reactions associated with chloride depletion in sea-salt particles and water-soluble organic matter (WSOM). The $g(90\%)$ maximized in summer and minimized in spring. The decrease in spring was most likely explained by the formation of less hygroscopic salts or particles via organometallic reactions during the long-range transport of Asian dust. Cl^- and Na^+ dominate the mass fractions of WSM, followed by nss-SO_4^{2-} and WSOM. Based on regression analysis, we confirmed that $g(90\%)$ at Chichijima Island largely increased due to the dominant sea spray; however, atmospheric processes associated with chloride depletion in sea salts and WSOM often suppressed $g(90\%)$. Furthermore, we explored the deviation (average: 18%) between the measured and predicted $g(90\%)$ by comparing measured and model growth factors. The present study demonstrates that long-range atmospheric transport of anthropogenic pollutants (SO_2, NO_x, organics, etc.) and the interactions with sea-salt particles often suppress the hygroscopic growth of marine aerosols over the western North Pacific, affecting the remote background conditions.

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* Corresponding author at: Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan.
E-mail address: kawamura@lowtem.hokudai.ac.jp (K. Kawamura).

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The present study also suggests that the HCl liberation leads to the formation of less hygroscopic aerosols over the western North Pacific during long-range transport.

1. Introduction

Particle hygroscopicity is a key property of atmospheric aerosols that affects the magnitude of aerosol radiative forcing. Based on modeling, aerosol particles are considered to have a cooling effect on a global scale (-1.2 W m^{-2}) despite the large uncertainty (-1.5 to $+0.8$ W m^{-2}). Incomplete knowledge of particle hygroscopic growth is the main source of uncertainty (IPCC, 2013). In addition to its effect on radiative transfer, hygroscopicity is also relevant to aqueous phase reactions in the atmosphere, in which the condensed water serves as the reaction medium (Mogili et al., 2006). Moreover, the hygroscopic growth of particles that are exposed to high relative humidity (RH) can substantially decrease the visibility (Chen et al., 2012).

Sea-spray particles are important in atmospheric chemistry and radiative transfer in the lower troposphere (O'Dowd et al., 1997; Rossi, 2003). Sea-salt particles (NaCl) are characterized by high hygroscopic deliquescence and are mainly produced by the evaporation of sea spray. The production rate of sea-salt particles is governed by wind speed and foam cover (Blanchard and Woodcock, 1980). As a result of the reactions between sea salt and inorganic and organic species (mixing state), numerous species such as HCl, chlorine, nitrogen oxide compounds and many organic species are released to the gas phase and frequently detected in the marine atmosphere (Kawamura et al., 1996; Kerminen et al., 1998; Laskin et al., 2002; Laskin et al., 2012; Ma et al., 2013). Therefore, knowledge of the aerosol mixing state is necessary for modeling studies on the hygroscopic (Okada et al., 2005) and optical properties (Pósfai et al., 1999) of particles and for providing information about their atmospheric processes (aging and reactions) (Li et al., 2003; Pósfai et al., 2003) and sources (Niemi et al., 2004). Nonetheless, the effect of the mixing state on the hygroscopicity of marine aerosols remains unclear.

Most mineral dusts in the troposphere originate from the dust belt, a chain of arid regions that include the Sahara Desert and deserts in Middle East and East Asia (Posfai and Buseck, 2010). Gong et al. (2003) reported that the principal source regions of dust in East Asia are the Taklimakan Desert in Xinjiang Province and the desert regions of Mongolia, including the Gobi desert. Based on surface measurements in Beijing, Matsuki et al. (2005) classified 28% of the Asian dust particles as calcite. The heterogeneous chemistry on mineral dust particles can alter the physicochemical properties of individual particles by the gas-to-particle conversion during long-range atmospheric transport (Bian and Zender, 2003; Jacob, 2000; Laskin et al., 2005; Sullivan et al., 2009). Creamean et al. (2013) reported that dust and biological particles from Asia affect precipitation in the western U.S. The degree of aging of dust particles depends on the precise mixture of dust and pollutants (anthropogenic) and their transport distance (Itahashi et al., 2010; Tobo et al., 2010; Wang et al., 2013). Therefore, investigations of East Asian aerosol particles and their transport over the western North Pacific are crucial for better understanding the atmospheric impact on a global scale.

The remote island of Chichijima is located in the western North Pacific over the outflow region of Asian dust and polluted air masses from China (Wang et al., 2009). Therefore, this site is suitable for studying the long-range atmospheric transport of air pollutants in East Asia and the anthropogenic activity under marine background conditions during winter and spring (see Fig. S1 in Supporting information). In this study, we investigated the temporal and seasonal variations in the hygroscopicity of aerosol particles generated by nebulization of water extracts of total suspended particle (TSP) samples collected in Chichijima Island during January–September 2003. The hygroscopic growth factor g(RH) was measured at RH of 5–95% using a hygroscopic tandem differential mobility analyzer (HTDMA) with an initial dry particle diameter of 100 nm. We discuss the link between hygroscopicity and aerosol chemical composition. Finally, we compare the measured and model growth factors over the sampling site.

2. Experimental

2.1. Aerosol sampling

TSPs were collected weekly at the Satellite Tracking Center of the Japan Aerospace Exploration Agency (JAXA, elevation: 254 m) in Chichijima Island (27°04′N and 142°13′E) 5 m above the ground during January–September 2003. The geographical location of the sampling site is shown in Fig. S1a. Aerosol particles were collected on precombusted (450 °C for 3 h) quartz filters (20 × 25 cm, Pallflex 2500QAT-UP) using a high-volume air sampler with flow rate of 1 m^3 min^{-1} (Kawamura et al., 2003). The filters were placed in a clean glass jar with a Teflon-lined screw cap before sampling. After sampling, the filters were recovered into the glass jar, transported to the laboratory in Sapporo, and stored in a freezer room at −20 °C prior to analysis. A total of 37 aerosol and 4 field blank samples were collected during the study period.

2.2. Analysis of chemical species

To determine inorganic ions (NH_4^+, SO_4^{2-}, NO_3^-, Na^+, Cl^-, K^+, Ca^{2+}, and Mg^{2+}), a punch (20 mm in diameter) from each filter was extracted with 10 mL organic-free and deionized ultrapure water. These extracts were passed through a disk filter (Millex-GV, 0.22 μm in pore size, Millipore) after ultrasonication (15 min × 3 times). Major ions were measured using ion chromatography (761 Compact IC, Metrohm, Switzerland) (Agarwal et al., 2010; Boreddy and Kawamura, 2015).

To determine water-soluble organic carbon (WSOC), a punch (20 mm in diameter) of each quartz fiber filter was extracted with 20 mL organic-free ultrapure water (resistivity of >18.2 MΩ cm, Sartorius arium 611 UV) under ultrasonication. These extracts were passed through a syringe filter (Millex-GV, 0.22 μm in pore size, Millipore) and analyzed using a total organic carbon (TOC) analyzer (Shimadzu, TOC-5000A) (Aggarwal and Kawamura, 2008). The atmospheric concentrations of water-soluble organic matter (WSOM) were estimated by multiplying measured WSOC with a factor of 2.1 (Aggarwal et al., 2007).

The analytical error in the replicate analyses was <10%. The detection limit of water-soluble ions was about 0.1 ng m^{-3} (Kunwar and Kawamura, 2014). The concentrations of all water-soluble species are corrected for field blanks that were collected during the sampling period.

2.3. Evaluation of non-sea salt components

The contributions from other sources excluding sea-salts are calculated using Na^+ as a sea spray marker (Keene et al., 1986). The mass concentrations of non-sea-salt (nss) components are estimated as (Guo et al., 2011):

$$\text{nss-SO}_4^{2-}\ (\mu\text{g m}^{-3}) = \left[\text{SO}_4^{2-}\right] - 0.245 \times \left[\text{Na}^+\right] \tag{1}$$

$$\text{nss-K}^+\ (\mu\text{g m}^{-3}) = \left[\text{K}^+\right] - 0.035 \times \left[\text{Na}^+\right] \tag{2}$$

$$\text{nss-Ca}^{2+}\ (\mu\text{g m}^{-3}) = \left[\text{Ca}^{2+}\right] - 0.037 \times \left[\text{Na}^+\right]. \tag{3}$$