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Hygroscopic behavior of water-soluble matter in marine aerosols over the East China Sea

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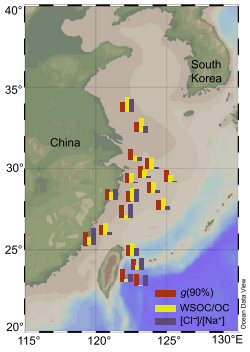
HIGHLIGHTS

- Hygroscopic behaviors of water-soluble matter were measured in marine aerosols over the East China Sea.
- The transport of anthropogenic pollutants strongly influenced the $g(90\%)$.
- Chemical aging processes could form some less hygroscopic components altering the $g(90\%)$.
- Higher $g(90\%)$ in the nighttime was related to enhanced heterogeneous reaction and higher Cl^-/Na^+ molar ratios.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we investigated hygroscopic properties of water-soluble matter (WSM) in marine aerosols over the East China Sea, which were collected during a Natural Science Foundation of China (NSFC) sharing cruise in 2014. Hygroscopic growth factors (g) of WSM were measured by a hygroscopicity tandem differential mobility analyzer (H-TDMA) with an initial dry particle mobility diameter of 100 nm. The observed g at 90% relative humidity (RH), $g(90\%)_{WSM}$, defined as the ratio of the particle diameter at 90% RH to that at RH < 5% (initial dry diameter), ranged from 1.67 to 2.41 (mean ± std: 1.99 ± 0.23). The g values were lower than that of seawater (2.1) but comparable with those reported for marine aerosols (1.79–2.08). The H-TDMA retrieved hygroscopicity parameter of WSM, κ_{WSM}, ranged from 0.46 to 1.56 (0.88 ± 0.35). The observed $g(90\%)_{WSM}$ during the daytime ranged from 1.67 to 2.40 (1.95 ± 0.21) versus 1.71 to 2.41 (2.03 ± 0.26) during the nighttime. κ_{WSM} was 0.81 ± 0.32 in the daytime and 0.95 ± 0.40 in the nighttime. The day/night differences of $g(90\%)_{WSM}$ and κ_{WSM} indicated that nighttime marine aerosols were more hygroscopic than those in daytime, which was likely related to enhanced heterogeneous reaction of ammonium nitrate in nighttime and the higher Cl^-/Na^+ molar ratios obtained (0.80) in nighttime than those (0.47)

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in daytime. Inorganic ions accounted for 72–99% of WSM with SO_4^{2-} being the dominant species, contributing to 47% of the total inorganic ion mass. The declined g(90%) comparing with sea water was likely due to the transport of anthropogenic aerosols, chemical aging of dust particles, the contribution of biomass burning products, and the aerosol hygroscopic growth inhibition of organics.

1. Introduction

Marine aerosols contribute significantly to the global natural aerosol system and have been regarded as an important factor influencing the Earth's albedo and regional climate by participating in various atmospheric processes (Charlson et al., 1987; Ramanathan et al., 2001). For example, marine aerosols perturb the radiative forcing of the Earth directly by scattering and absorbing the incoming sunlight or indirectly by acting as cloud condensation nuclei (CCN) and thus altering their water uptake properties (Charlson et al., 1991; Twomey, 1977). Knowledge of the physical and chemical properties of aerosols is important, because of their role in Earth's radiation balance, fog formation and cloud physics, and visibility degradation as well as human health. The determination of physical and chemical properties of aerosol particles is necessary for these effects (Massling et al., 2003). Therefore, detailed information on the physical and chemical properties of marine aerosols is crucial for the aerosol studies.

The hygroscopic behavior of aerosol particles plays a significant role in determining their size and physical properties. The hygroscopicity of atmospheric aerosol particles responding with the size of the particles at ambient relative humidity is important for aerosol optical properties (scattering and absorption), radiative forcing and residence time of these particles (Boreddy and Kawamura, 2015; Massling et al., 2003; Meskhidze and Nenes, 2006; O'Dowd et al., 2004). Furthermore, the hygroscopic behavior of atmospheric particles has been considered to be involved with the number of CCN, and thus determine the resulting droplet size distribution of cloud, which in turn affects cloud albedo (Good et al., 2010; Pringle et al., 2010; Twomey, 1974). The impact of aerosol particles in the marine boundary layer is potentially high, because the oceans cover >70% of the Earth's surface and clouds in this layer are estimated to control about one-third of the Earth's albedo (Charlson et al., 1987). In addition, aerosol hygroscopicity provides information about the mixing state and the chemical components of aerosol particles (Massling et al., 2003).

Hygroscopic behaviors of aerosol particles have been investigated at different locations, e.g., the Pacific and Southern Oceans (Berg et al., 1998), the Atlantic and Indian oceans (Massling et al., 2003), Yosemite National Park, USA (Carrico et al., 2005), Ulaanbaatar (Jung et al., 2011), the Chichijima Island in the western North Pacific (Boreddy et al., 2014a), a rural site in Tanzania (Boreddy et al., 2014b), and urban Hong Kong (Cheung et al., 2015). Currently, the atmospheric environment of China is changing rapidly due to increased industrialization and urbanization. The East China Sea is one of the largest marginal seas in the world. It is situated between the western North Pacific and the east coast of China, where human activities impose a heavy loading into the atmosphere (Fu et al., 2011; Hatakeyama et al., 2004; Nakamura et al., 2005). Previous studies have reported water soluble inorganic ions (Hatakeyama et al., 2004), water soluble organic nitrogen (Nakamura et al., 2006), carbonaceous species (Wang et al., 2015), and trace elements (Hsu et al., 2010) in aerosol samples from the East China Sea and the western North Pacific. However, up to now, little is known about hygroscopic properties of marine aerosols from this region, where is heavily influenced by the outflow of Asian aerosols.

In this study, we examined the hygroscopic properties of the particles with an initial diameter of 100 nm, which were formed by nebulization of water extracts in total suspended particles (TSP) from the East China Sea using a hygroscopicity tandem differential mobility analyzer (H-TDMA). Water-soluble inorganic ions, carbonaceous components and levoglucosan were also examined to investigate their potential influences on the hygroscopicity of marine aerosols.

2. Experiment and analysis

2.1. Aerosol sampling

The studied region is located within 119°E–126°E and 22°N–35°N in the East China Sea (ECS). The aerosol sampling was conducted on board the vessel NORC2014-02 during a National Natural Science Foundation of China (NSFC) sharing cruise from May 18 to June 12, 2014. Samples of total suspended particles (TSP) were collected on precombusted (450 °C for 6 h) quartz filters (PALLFLEX 2500QAT-UP, 20 × 25 cm) using a high-volume sampler (Kimoto AS-810B) at a flow rate 0.6 m^3 min^{-1}. The sampler was mounted on the upper deck of the ship, 8 m above the sea surface. The sampling duration was about 12 h. After sampling, the filters were kept separately in the precleaned glass jar with a Teflon-lined screw cap, transported to the laboratory, and stored at −20 °C prior to analysis. In total, eighteen aerosol filter samples were measured in the present study (Fig. 1).

2.2. Measurement of chemical species

Inorganic ions (NH_4^+, SO_4^{2-}, NO_3^-, Na^+, Cl^-, K^+, Ca^{2+}, and Mg^{2+}) and methanesulfonate (MSA^-) were extracted from a punch (20 mm in diameter) of the filter samples with 10 mL organic-free ultrapure water (resistivity of >18.2 MΩ cm, 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 Boreddy and Kawamura (2015).

To determine water-soluble organic carbon (WSOC), a punch of 20 mm diameter from each quartz fiber filter was extracted with 15 mL organic-free ultrapure water (resistivity of >18.2 MΩ cm, Sartorius arium 611 UV) 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) (Boreddy et al., 2014a).

A filter punch of 20 mm diameter from each filter was used to determine the concentrations of organic carbon (OC) and elemental carbon (EC) using a Sunset Lab carbon analyzer, following the Interagency Monitoring of Protected Visual Environments (IMPROVE) method (Wang et al., 2005). Duplicate analyses of filter samples showed uncertainties of ±10%.

For the determination of levoglucosan (LG), a filter sample (1.54 cm^2) was extracted three times with dichloromethane/methanol (2:1; v/v) under ultra-sonication for 10 min firstly. The sugar compounds in the solvent extracts were then derived to trimethylsilyl ethers by reacting with 50 μL of *N*,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethylsilyl chloride and 10 μL of pyridine at 70 °C for 3 h. After the reaction, the derivatives were diluted by addition of 140 μL of n-hexane containing 1.43 ng μL^{-1} internal standard (C_{13} n-alkane). Finally, the fragment ions of m/z 217 and 204 were used for the quantification of LG (Fu et al., 2011).

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