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Seasonal variabilities in chemical compounds and acidity of aerosol particles at urban site in the west Pacific☆

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ABSTRACT

Mass concentrations of chemical compounds in both $PM_{2.5}$ (particle aerodynamic diameter, $Dp < 2.5\ \mu m$) and $PM_{2.5\text{-}10}$ ($2.5 < Dp < 10\ \mu m$), and acidity of aerosol particles were measured at an urban site in western Japan using a continuous dichotomous Aerosol Chemical Speciation Analyzer (ACSA-12) throughout 2014. Mass concentrations of both $PM_{2.5}$ and sulfate had distinct seasonal variabilities with maxima in spring and winter, mostly due to long-range transport with the prevailing westerly wind. Mass concentration of nitrate in $PM_{2.5}$ (fNO_3) showed an obvious warm-season-low and cold-season-high pattern as a result of both gas-aerosol phase equilibrium processes under high temperature conditions as well as transport. Nitrate in $PM_{2.5\text{-}10}$ (cNO_3) increased during long-range transport of dust, implying the great importance of heterogeneous processes at the surface of coarse mode particles. In this study, $\Delta[H^+]$ (derived from the difference in pH of extract liquid with/without sampling) was used to indicate the acidity of particles. We found that acidity of particles in $PM_{2.5}$ ($f\Delta H$) was mostly positive with a maximum in August because of the large fraction of nitrate and sulfate. Acidity of particles in $PM_{2.5\text{-}10}$ ($c\Delta H$) was negative in winter and spring due to presence of alkaline matter from crustal sources. This study highlights the great importance of anthropogenic pollutants on the acidity of particles in the western Pacific Ocean and further impact on the marine environment and climate.

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1. Introduction

In East Asia, substantial emissions of primary pollutants (NO_x, SO_2, CO, NMHCs, and anthropogenic dust) and secondary formation of anthropogenic aerosols (sulfate, nitrate, and organic aerosols) as a result of massive energy consumption have recently resulted in consecutive severe haze pollution events (Lawrence and Lelieveld, 2010; Wang et al., 2014; Li et al., 2017). Long-range transport (LRT) of anthropogenic pollutants in some episodic events also affected adherence to the National Ambient Air Quality Standard (NAAQS) in East Asian countries (Itahashi et al., 2017), and even along the west coast of North America (Zhang et al., 2008). In recent years, the issue of cross-boundary transport of particulate matter with an aerodynamic diameter of less than 2.5 μm ($PM_{2.5}$) has attracted great attention in both the scientific community and governments. The Kyushu area in Japan was frequently subjected to the cross-boundary transport of pollutants, and was more affected by the $PM_{2.5}$ issue than other parts of Japan (such as the Kanto region), especially during the cold season when westerly winds prevailed (Kaneyasu et al., 2014). For instance, model simulation studies at Fukue island (a remote marine site, 32.7 N, 128.68 E) demonstrated that central north China (105°E–124°E, 34°N–42°N) was mostly responsible for the increase in the ambient loading of $PM_{2.5}$, except during the summer (Ikeda et al., 2014). However (Kaneyasu et al., 2014), found that nitrate and elemental carbon differed substantially between Fukue island and urban sites in the Kyushu area, though the overall $PM_{2.5}$ concentration were almost identical. It has long been reported that non-sea-salt sulfate concentration in Japan is mainly influenced by LRT of secondary pollutions as a result of

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substantial SO_2 emissions from coal burning within continental Asian continent (Itahashi et al., 2014). In the past decades, implementation of desulfurization activities in China has evidently reduced the tropospheric sulfate concentration in East Asia (Kurokawa et al., 2013). However, the transport issue of nitrate remains unclear, especially in metropolitan areas where nitrate formation from local NO_x emissions were ubiquitously evident. Besides, coexistence of NO_x with SO_2, leading to the rapid conversion of SO_2 to sulfate, accelerated the formation of secondary particles (He et al., 2014). Recent studies on cross-boundary transport of pollution cases over East Asia in January of 2015 demonstrated that both counterpart ion (such as NH_3) and aqueous-phase production of SO_4^{2-} during the transport had great impact on the outreach capacity of aerosol phase nitrate (Itahashi et al., 2017).

Previous studies have shown that mineral dust aerosols served as good carriers of nitrate in East Asia since the dust source regions (Taklimakan and Gobi desert) are close to populated/industrial areas in mainland China (Itahashi et al., 2010; Wang et al., 2017). The formation of nitrate on dust aerosols has been clearly observed using scanning electron microscopy (SEM) both in laboratory experiments and field measurements (Li and Shao, 2009). In principle, nitrate in the coarse mode is represented by the form of calcium nitrate ($Ca(NO_3)_2$) and magnesium nitrate ($Mg(NO_3)_2$) since gaseous nitric acid (HNO_3) is a very sticky molecule in the troposphere. A recent study in Japan showed that the nitrate mass in coarse mode increased by a factor of 5 during a long lasting dust event (Pan et al., 2015), and the water-soluble coatings on the surface of dust particles could lead to its morphological changes (Pan et al., 2017). In the marine region, HNO_3 tends to react with sea salt (e.g., NaCl) to produce $NaNO_3$ (aq) and gaseous HCl(g), resulting in the presence of NO_3^- in the coarse mode (Itahashi et al., 2016). reported coarse nitrate produced via sea salt was of particular importance as atmospheric input to East Asia oceans.

The acidity of particles is an important parameter to describe the availability that ambient acidic matter (such as sulfate, nitrate) is neutralized by ambient ammonia and other basic compounds. It directly related to environmental and health effects of atmospheric aerosols since acidic particles that deposited on the earth's surface will cause construction corrosion of building and soil acidification. Numbers of studies (He et al., 2012) used the ammonium-to-sulfate ratio of ambient aerosol to indicate the extent of neutralization because the concentrations of these two species were easily obtained. One applicable parameter is Strong acidity in terms of nmol $[H^+]/m^3$. It is obtained from the total $[H^+]$ derived from strong acids in an aqueous extract of aerosol samples that are dissolved in large excesses of water. Hence, it did not indicate the *in-situ* characteristics of ambient aerosols. Another parameter is *in-situ* aerosol acidity that reflects the concentration of free $[H^+]$ in the deliquesced particles at the ambient condition. It was normally estimated from a variety of thermodynamic models (E-AIM etc.). In this study, the acidity of particles was determined similar to the strong acid method.

The model simulation on the formation and transport of fine mode nitrate has been studying in East Asia (Uno et al., 2007, 2017; Itahashi et al., 2017); however, the tempo-spatial distribution of coarse mode nitrate remains unclear, and the corresponding contribution of cross-boundary transport has not been discussed. In the present study, we report the seasonal/diurnal variation in mass concentration of anthropogenic pollutants at an urban site of west Pacific, and investigate the controlling factors on allocation of aerosol phase nitrate between fine mode and coarse mode. Furthermore, acidity of particles was also studied on the basis of on-line measurement in order to better understanding the environmental/climate effect of anthropogenic pollutants in the East Asia.

2. Observations

Continuous observations of particulate matter (PM) and anthropogenic pollutant compounds (e.g., sulfate, nitrate, water-soluble organic compounds, and black carbon) in both fine (particle diameter, $Dp < 2.5\ \mu m$, identified as $PM_{2.5}$) and coarse mode ($2.5 < Dp < 10\ \mu m$, identified as $PM_{2.5-10}$) were performed using a continuous dichotomous Aerosol Chemical Speciation Analyzer (ACSA-12, Kimoto electric co. Ltd) at a time-resolution of 1 h from October 2013 to December 2014. The instruments were installed at the roof of a three-floor building in the Fukuoka Institute of Health and Environmental Sciences (Lat: 33.51°N, Lon: 130.50°E) before September 2014, and were then moved to a six-floor building in the Chikushi campus of Kyushu University (Lat: 33.52°N, Lon: 130.47°E). The NO_x emission from anthropogenic activities was limited in the surrounding area at the both sites. Geographic location and topography of observation sites were shown in Fig. 1. ACSA-12 was designed to continuously measure mass concentrations of PM and water-soluble species at a specified time resolution and at a flow rate of 16.7 L/min. The mass concentrations of $PM_{2.5}$ and $PM_{2.5\text{-}10}$ were determined using the beta-ray absorption method. The mass concentrations of nitrate ions and water-soluble organic compounds were determined using the ultra-violet absorption-photometric method. The mass concentration of sulfate ions was determined using the $BaSO_4$-based turbidimetric method after the addition of $BaCl_2$ dissolved in a polyvinyl pyrrolidone solution. The mass concentration of black carbon was determined optically using the near-infrared spectroscopy method; henceforth defined as OBC. The uncertainty of the instrument was estimated to be less than 10% (Kimoto et al., 2013; Pan et al., 2016a,b; Uno et al., 2017). In this paper, the mass concentrations of nitrate, sulfate, water soluble organic carbon in both $PM_{2.5}$ and $PM_{2.5\text{-}10}$ were marked as fNO_3, cNO_3, fSO_4, cSO_4, fWSOC and cWSOC, respectively.

The acidity of particles (marked as $\Delta[H^+]$, representing the difference between measured and standard solution) was also determined based on an absorption spectrometric method after adding the pH indicator. The basic equation is $pH_{solution} = -\log[\Delta H^+ \times 10^{-6} + 10^{-4.6}]$. Here pH solution is the pH value of aqueous extracts of aerosol sample, and the extract solvent has a pH of 4.6. The details of the ACSA instrument have been published in literature (Kimoto et al., 2013). Correspondingly, the acidity of particles in $PM_{2.5}$ and $PM_{2.5\text{-}10}$ were marked as $f\Delta H$ and $c\Delta H$.

Furthermore, light-polarization properties and size distribution of single particles at the observation site were measured using a Polarization Optical Particle Counter (POPC). The depolarization ratio (DR), denoted as the ratio of the intensity of the s-polarized signal to the total intensity of the backward-scattering signal, was adopted to indicate the sphericity/non-sphericity of aerosol particles. A detailed description of POPC was reported previously (Kobayashi et al., 2014; Pan et al., 2015, 2016b, 2017).

3. Results and discussions

3.1. Seasonal patterns

Mass concentrations of $PM_{2.5}$, $PM_{2.5-10}$, fNO_3, cNO_3, fSO_4, fWSOC, and $f\Delta H$ showed clear seasonal variabilities, as shown in Fig. 2. Monthly variations in mass concentrations of $PM_{2.5}$ showed a bimodal distribution with two peaks during January ($26.8 \pm 14\ \mu g/m^3$) and May ($31.5 \pm 15\ \mu g/m^3$), with minimum concentrations observed during August ($10.4 \pm 6.8\ \mu g/m^3$), as shown in Fig. 2a. Mass concentration of $PM_{2.5-10}$ showed a pronounced peak ($28.3 \pm 25\ \mu g/m^3$) in May due to the frequent impact of dust events in 2014 (Fig. 2b). Mass concentrations of fNO_3 during the cold season (DJF) were much higher than during the warm season (JJA)

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