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Significant geographic gradients in particulate sulfate over Japan determined from multiple-site measurements and a chemical transport model: Impacts of transboundary pollution from the Asian continent

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ABSTRACT

We found a significant geographic gradient (longitudinal and latitudinal) in the sulfate (SO_4^{2-}) concentrations measured at multiple sites over the East Asian Pacific Rim region. Furthermore, the observed gradient was well reproduced by a regional chemical transport model. The observed and modeled SO_4^{2-} concentrations were higher at the sites closer to the Asian continent. The concentrations of SO_4^{2-} from China as calculated by the model also showed the fundamental features of the longitudinal/latitudinal gradient. The proportional contribution of Chinese SO_4^{2-} to the total in Japan throughout the year was above 50–70% in the control case, using data for Chinese sulfur dioxide (SO_2) emission from the Regional Emission Inventory in Asia (40–60% in the low Chinese emissions case, using Chinese SO_2 emissions data from the State Environmental Protection Administration of China), with a winter maximum of approximately 65–80%, although the actual concentrations of SO_4^{2-} from China were highest in summer. The multiple-site measurements and the model analysis strongly suggest that the SO_4^{2-} concentrations in Japan were influenced by the outflow from the Asian continent, and this influence was greatest in the areas closer to the Asian continent. In contrast, we found no longitudinal/latitudinal gradient in SO_2 concentrations; instead SO_2 concentrations were significantly correlated with local SO_2 emissions. Our results show that large amounts of particulate sulfate are transported over long distances from the East Asian Pacific Rim region, and consequently the SO_4^{2-} concentrations in Japan are controlled by the transboundary outflow from the Asian continent.

1. Introduction

Particulate sulfate (SO_4^{2-}) in the atmosphere plays an important role in atmospheric physics and chemistry. In terms of climate change, particulate sulfate has negative radiative forcing (Intergovernmental Panel on Climate Change IPCC, 2001). SO_4^{2-} is one of the most dominant constituents of fine particles in the atmosphere. $(NH_4)_2SO_4$ and NH_4HSO_4 are representative atmospheric sulfates, and they are important as condensation nuclei as well as air pollutants.

SO_4^{2-} in the atmosphere is controlled by chemical production, transport, and deposition. It is produced from chemical reactions involving gaseous precursors (e.g., sulfur dioxide [SO_2], dimethyl sulfide [DMS]), except for sea-salt SO_4^{2-} and that from gypsum dust particles. SO_4^{2-} is scavenged from the atmosphere by wet and dry deposition processes. Wet deposition accounts for more than 80% of SO_4^{2-} removal from the atmosphere (IPCC, 2001). Because SO_2 is one of the main anthropogenic precursors of SO_4^{2-}, it is important to study SO_2 and SO_4^{2-} simultaneously when studying the atmospheric chemistry of SO_4^{2-}.

SO_4^{2-} in East Asia has been gaining increased international attention in conjunction with the increasing energy consumption and SO_2 emissions in the region (e.g., Shimohara et al., 2001; Hong et al., 2002). The emissions of air pollutants such as SO_2 and nitrogen oxides (NO_x) in Asia have become comparable to those in

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North America and Europe (Akimoto, 2003), and they will continue to increase in response to industrial development and population growth in the region. The growth of China's population to more than 1.3 billion and its rapid economic growth have contributed to the increased energy consumption and emission of air pollutants in the region. It is anticipated that without effective countermeasures, SO_2 emissions in China will continue to increase and by 2020 will be 48% higher than 2000 levels (Ohara et al., 2007). This suggests that both acid deposition and air pollution will become more serious in Asia.

The Japan Environmental Laboratories Association (JELA) has been conducting an acid deposition survey since 1991, scientifically studying acid deposition in Japan and publishing numerous reports (e.g., JELA, 2007). A review of the JELA data set by Aikawa et al. (2008) indicated that the concentrations of atmospheric SO_2 were affected by the 2000 eruption of Mt. Oyama (the Miyakejima Volcano), but no effects on SO_4^{2-} concentrations were observed, and that the SO_4^{2-} concentrations in their study area (a 250 × 250 km region of Japan) were within or slightly higher than the range of concentrations determined by the European Monitoring and Evaluation Programme (EMEP) or those in mid-latitude North America. They suggested that the SO_4^{2-} concentration might be controlled on a continental or hemispherical scale. However, the data set that they studied was limited to data from the central part of Japan, whereas Japan covers a large distance from north to south and from east to west (about 2500 × 2500 km). Aikawa et al. (2006) also observed the transboundary transport of an air mass with high SO_4^{2-} concentration from the Eurasian continent to Japan. These studies highlight the outflow of SO_4^{2-} from the Eurasian continent, although they were conducted in a limited area or at a specific site.

Recently, air quality over northeastern Asia, including Japan, has been declining because of the increasing emissions of SO_2, NO_x, and other air pollutants from Asia (Naja and Akimoto, 2004; Uno et al., 2007; Ohara et al., 2008). Studies using chemical transport models show that air pollutants such as sulfur and nitrogen depositions (Lin et al., 2008a,b), particulate nitrogen and nitrogen deposition (Uno et al., 2007), and tropospheric ozone (Tanimoto et al., 2005; Yamaji et al., 2006, 2008) are transported long distances from the Asian continent to the Japanese Islands. Some intensive experiments, such as the Aerosol Characterization Experiments (ACE)-Asia and the National Aeronautics and Space Administration (NASA) Transport and Chemical Evolution over the Pacific (TRACE-P), have been conducted to investigate the long-range transport of air pollutants and the impacts of Asian continental outflows on the Northwestern Pacific atmosphere (e.g., Huebert et al., 2003; Jacob et al., 2003; Zhang et al., 2004; Kurata et al., 2004; Kim et al., 2005, 2007; Song et al., 2007). In addition, the long-range transport of East Asian SO_4^{2-} to Canada was investigated in the Intercontinental Chemical Transport Experiment, Phase B (INTEX-B) (Van Donkelaar et al., 2008). Such experiments have clarified the extent of long-range transport from East Asia and the impacts to North America and the rest of the northern hemisphere. Liu et al. (2008) analyzed the effect of varying East Asian sulfur emissions on sulfate concentrations in the northern hemisphere, and determined that East Asian sulfate contributed approximately 20–80% of northern hemisphere sulfate. Saikawa et al. (2009) also showed that the contribution from China to sulfate aerosol concentrations was large, especially over Japan. In addition, some other studies have looked closely at the intercontinental transport of atmospheric pollutants (Liu and Mauzerall, 2007; Liu et al., 2009a,b). The results of all of these studies strongly suggest the large influence of the outflow from the Asian continent over Japan.

In the present study, we used the 4-stage filter-pack method for the simultaneous measurement of SO_2 and SO_4^{2-} concentrations at multiple sites throughout Japan for 3 years, from April 2003 to March 2006. We used the measurements at multiple sites to determine the spatial and seasonal variations of SO_4^{2-} concentrations. In particular, we focused on the significant longitudinal and latitudinal gradients in the SO_4^{2-} concentration, and used a regional chemical transport model to examine the implications of these gradients.

2. Methods

2.1. Measurement of SO_2 and SO_4^{2-}

2.1.1. Measurement locations and site classification

Our survey was conducted at 32 sites established by JELA and located in urban, suburban, and rural areas of Japan (Table 1, Fig. 1). For the present study, we used a 3-y data set (Japan Fiscal Year [FY; April–March] 2003–2005).

Local SO_2 emissions around the monitoring sites were classified into 3 categories: 'S' (<80 t ha^{-1} y^{-1}), 'M' (80–422 t ha^{-1} y^{-1}), and 'L' (>422 t ha^{-1} y^{-1}). We estimated the SO_2 emissions for the area within a radius of about 20 km of the monitoring sites from available 10-km × 10-km mesh data (Japan Environmental Laboratories Association, 2007).

2.1.2. Sample collection and chemical analysis

We used the 4-stage filter-pack method to collect SO_2 and SO_4^{2-} (stage 1: PTFE filter; stage 2: polyamide filter; stage 3: 6% (wt:wt) K_2CO_3–2% (wt:wt) glycerin-impregnated filter; and stage 4: 5% (wt:wt) H_3PO_4–2% (wt:wt) glycerin-impregnated filter) (Karakas and Tuncel, 1997; Matsumoto and Okita, 1998; Sickles et al., 1999). In this method, SO_2 is collected mainly by the K_2CO_3–glycerin-impregnated filter, and partially by the polyamide filter. SO_4^{2-} is collected by the PTFE filter. The filter holder is a NILU (Norwegian Institute for Air Research, Kjeller, Norway) open-face filter holder. The samples were collected weekly (Monday–Monday). The flow rate for sampling was usually about 1.0 L min^{-1}, although at several sites it was 2.0–5.0 L min^{-1}. This method can also be used to collect other gases such as HNO_3, HCl, and NH_3, and other aerosols such as NO_3^-, Cl^-, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}. The most serious drawback of the 4-stage filter-pack method is the possibility of generating artifacts (e.g., Matsumoto and Okita, 1998). However, few sampling artifacts have been observed for sulfur compounds (Sickles et al., 1999; Matsuda et al., 2002). The data assessment for the sample collection was carried out on the basis of the sampling flow rate; the detailed methodology is described in previous reports (Aikawa et al., 2005; Japan Environmental Laboratories Association, 2007).

The PTFE filter, polyamide filter, and 5% H_3PO_4–2% glycerin-impregnated filter were extracted using deionized water. The 6% K_2CO_3–2% glycerin-impregnated filter was extracted using a 0.03% H_2O_2 solution to thoroughly oxidize SO_2 (SO_3^{2-}) to SO_4^{2-}. The extracts were filtered through a 0.45-μm pore-size membrane filter and measured using an ion chromatograph.

2.1.3. Data set

The data from 3 years at the 32 monitoring sites were analyzed on the basis of monthly, annual, or 3-y means, although the samples were collected weekly. At some sites, some weekly or monthly data were missing because of sampling problems. As a result, 10 annual mean values at these sites could not be calculated (Table 1). These missing data might have introduced some biases in comparisons of 3-y mean values. To check for any biases, we compared the 3-y mean data for two cases. In Case I, the data sets at all sites were used, even though some data were missing. In Case II, we excluded the data from sites with incomplete annual data sets. A comparison of the statistics for Cases I (32 sites) and II (24 sites) shows a maximum difference in both mean and median