NOTE

Ten-year observation of sulfur isotopic composition of sulfate in aerosols collected at Tsuruoka, a coastal area on the Sea of Japan in northern Japan

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Atmospheric aerosol samples were collected from 1993 to 2003 at Tsuruoka, Japan, a coastal area on the Sea of Japan. Concentration of water-soluble chemical components and sulfur isotopic ratios of sulfate in aerosol samples were measured to evaluate the temporal variation and identify the source. The samSO_4^{2-} and nssSO_4^{2-} concentrations range from 7.6 to 354.4 and 3.7 to 335.6 neq m^{-3} , respectively, and there was no clear seasonal variation. Sulfur isotope ratios of total sulfate ($\text{sam}\delta^{34}\text{S}$) and non-sea salt sulfate ($\text{nss}\delta^{34}\text{S}$) in aerosols are +1.0 to +15.1 with a mean value of +5.7‰ and −4.4 to +14.5 with a mean value of +4.1‰, respectively. The values of $\text{sam}\delta^{34}\text{S}$ and $\text{nss}\delta^{34}\text{S}$ are relatively low in summer and high in the other three seasons. The $\text{nss}\delta^{34}\text{S}$ values of aerosols in fall to spring agree with the average sulfur isotope ratios of coal used in northern China, considering the isotope fractionation. These results indicate the possibility of long-range transport of sulfate from the Asian continent to Japan. The variations of atmospheric samSO_4^{2-} and nssSO_4^{2-} concentrations decreased gradually and reach a minimum in 1999. The decline of SO_2 emission in China due to reduction in industrial coal use, a slowdown of the Chinese economy, and the closure of small and inefficient plants would be among the causes of this decreasing observed trend. On the other hands, the variation ranges of $\text{sam}\delta^{34}\text{S}$ and $\text{nss}\delta^{34}\text{S}$ values abruptly changed after 2000. The introduction of fuel-gas desulfurization technologies to industrial plants of coke production and thermal power stations would be one of the most important causes of this change.

Keywords: long-term observation, aerosol, sulfate, $\delta^{34}\text{S}$

INTRODUCTION

Atmospheric pollution is one of the most serious environmental problems worldwide. In particular, sulfur dioxide (SO_2) originating from combustion of fossil fuels such as coal and petroleum is transformed to sulfate aerosols through oxidation reaction in the atmosphere, and the aerosols are scavenged from the atmosphere by rainout, washout, and dry deposition, before finally reaching the ground surface. Therefore, in addition to air pollution, they also cause acid rains.

Long-range transport of anthropogenic pollutants has caused serious environmental problems (Koçak *et al.*, 2004). In the Far East Asian region, including the Japanese archipelago, strong northwesterly winter monsoons from the Asian continent blow to Japan during winter and

spring. These monsoons carry air masses including suspended materials from near the surface of the Asian continent (Arndt and Carmichael, 1995). In the Asian countries, the amount of SO_2 released into the atmosphere by fossil fuel combustion has generally increased due to rapid economic growth (Guttikunda *et al.*, 2003). It is expected that atmospheric aerosols along the Sea of Japan area contain SO_2 emissions from the Asian continent brought by the winter monsoons. Therefore, it is important to understand the concentration level and contribution of long-range transported components in this area.

Sources of atmospheric sulfur compounds are: (1) sea spray SO_4^{2-} ; (2) anthropogenic sulfur such as SO_x ; (3) biogenic sulfur such as H_2S and DMS (dimethylsulfide); and (4) volcanic sulfur such as H_2S and SO_2 . To clarify the environmental sources of sulfur compounds, Nakai and Jensen (1967) attempted to apply the sulfur isotope ratio ($\delta^{34}\text{S}$) as a natural tracer. Since then, several groups have reported on the sulfur dynamics in the natural environment by using $\delta^{34}\text{S}$ values (Fuller *et al.*, 1986; Mukai *et al.*, 2001; Zhao *et al.*, 2003). It has been discussed that $\delta^{34}\text{S}$ values of non-sea salt sulfate in wet deposition along

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Fig. 1. Location of sampling point.

the Sea of Japan coast of Japan show a clear seasonal variation being high in winter and low in summer, and that $\delta^{34}\text{S}$ values of non-sea salt sulfate in winter wet depositions contain sulfur related to coal combustion in East Asia (Ohizumi *et al.*, 1997; Kawamura *et al.*, 2002). Akata *et al.* (2002) suggested that the main source of sulfur compounds in Japanese winter wet deposition was the Asian continent.

For approximately 10 years since 1993, we have monitored atmospheric aerosols at Tsuruoka, located on the Sea of Japan, and analyzed their chemical components and the $\delta^{34}\text{S}$ values of sulfate. We have already reported some of the $\delta^{34}\text{S}$ values (Motoyama *et al.*, 2000). In the present study, we report long-term variation of atmospheric SO_4^{2-} concentrations and $\delta^{34}\text{S}$ values of SO_4^{2-} in aerosols from the area facing the Sea of Japan in order to clarify the influence of long-range transported sulfur compounds.

MATERIALS AND METHODS

Sample collection

Sampling was made on top of a building of the Tsuruoka National College of Technology in Tsuruoka City, Yamagata Prefecture, Japan (38°42' N, 139°47' E), approximately 9 km away from the shore of the Sea of Japan and 20 m high above ground level (Fig. 1). Tsuruoka city is located on the western edge of the Shonai plain and is surrounded by high mountains. The sampling

method was identical to that we used previously (Motoyama *et al.*, 2000). Briefly, aerosol particles (TSP: total suspended particles) were collected during the period of November 1993 to December 2003, using a high-volume air sampler (HVC-1000; Sibata Scientific Technology Ltd.) on a 203 mm $\times$ 254 mm PTEF filter (PF040; Advantec) and/or quartz fiber filters (QR-100; Advantec). The airflow rate was 700 L min⁻¹. Sampling was made 334 times during 10 years, each of which consists of approximately 5-day sampling duration. In this study, we did not measure sample (aerosol particle) weight.

Analytical methods

A quarter of each filter was taken for extracting water-soluble components. The quarter filter was put into a Teflon vessel filled with distilled water. The water-soluble components were extracted ultrasonically for 5 min. The extracted solution was then filtered through a 0.45 μm membrane filter (C045A047A; Advantec).

The concentrations of Cl^- , NO_3^- , and SO_4^{2-} were measured by ion chromatography (2020i; Dionex). Concentrations of Na^+ were determined using ICP-AES (SPS7000A; Seiko Instruments Inc.).

After chemical analyses, SO_4^{2-} was precipitated as BaSO_4 from the extracted solution for $\delta^{34}\text{S}$ analysis. For the $\delta^{34}\text{S}$ analysis, the BaSO_4 precipitate was dried and converted to SO_2 through thermal decomposition using a mixture of SiO_2 – V_2O_5 in a vacuum line (Yanagisawa and Sakai, 1983). Subsequently, $\delta^{34}\text{S}$ was measured using a

Fig. 2. Relationship between atmospheric Na^+ and Cl^- equivalent concentrations in aerosol samples (●) and that of seawater ratio (dashed line: equivalent concentration ratio).

stable isotope ratio mass spectrometer (Optima; Micromass). The Canyon Diablo Troilite (CDT) scale was applied for reporting the $\delta^{34}\text{S}$ values, which is defined as

$$\delta^{34}\text{S} = \left(\frac{\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{sample}}}{\left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{std}}} - 1 \right) \times 1000 \quad (1)$$

where $^{34}\text{S}/^{32}\text{S}_{\text{sample}}$ and $^{34}\text{S}/^{32}\text{S}_{\text{std}}$ denote the $^{34}\text{S}/^{32}\text{S}$ ratios of sample and standard, respectively. The analytical precision, including the preprocessing operation, was better than $\pm 0.2\text{‰}$. We used BaSO_4 of NBS-127 ($\delta^{34}\text{S}_{\text{CDT}}: +20.32 \pm 0.36\text{‰}$) as secondary standard material. We obtained 178 data in total.

RESULTS AND DISCUSSION

Atmospheric concentration of SO_4^{2-} and $\delta^{34}\text{S}$ of sulfate in aerosols

Figure 2 shows the relationship of Na^+ and Cl^- concentration in aerosols with seawater ratio of Na^+ and Cl^- equivalent concentration. Almost all the samples are distributed along the sea water line, suggesting Na^+ and Cl^- originated from seawater. On the basis of Na^+ as the tracer for sea salt component, non-sea salt SO_4^{2-} ($_{\text{nss}}\text{SO}_4^{2-}$) concentration and $\delta^{34}\text{S}$ of non-sea salt sulfate ($_{\text{nss}}\delta^{34}\text{S}$) were calculated by the following equations:

$$_{\text{nss}}\text{SO}_4^{2-} = _{\text{sam}}\text{SO}_4^{2-} - \frac{_{\text{sea}}\text{SO}_4^{2-}}{_{\text{sea}}\text{Na}^+} \times _{\text{sam}}\text{Na}^+ \quad (2)$$

$$_{\text{nss}}\delta^{34}\text{S} = \frac{_{\text{sam}}\delta^{34}\text{S} \times _{\text{sam}}\text{SO}_4^{2-} - _{\text{sea}}\delta^{34}\text{S} \times (_{\text{sam}}\text{SO}_4^{2-} - _{\text{nss}}\text{SO}_4^{2-})}{_{\text{nss}}\text{SO}_4^{2-}} \quad (3)$$

where $_{\text{sam}}\text{SO}_4^{2-}$ and $_{\text{sam}}\text{Na}^+$ are SO_4^{2-} and Na^+ concentrations in each samples, $_{\text{sea}}\text{SO}_4^{2-}$ and $_{\text{sea}}\text{Na}^+$ are SO_4^{2-} and Na^+ concentrations in sea water, $_{\text{sam}}\delta^{34}\text{S}$ and $_{\text{sea}}\delta^{34}\text{S}$ are $\delta^{34}\text{S}$ values of sample and seawater ($+20.3\text{‰}$; Rees *et al.*, 1978).

Figure 3 shows the seasonal variations of $_{\text{sam}}\text{SO}_4^{2-}$ concentrations, $_{\text{nss}}\text{SO}_4^{2-}$ concentrations, and $_{\text{sam}}\delta^{34}\text{S}$ and $_{\text{nss}}\delta^{34}\text{S}$ values of aerosols. Concentrations of $_{\text{sam}}\text{SO}_4^{2-}$ and $_{\text{nss}}\text{SO}_4^{2-}$ range from 7.6 to 354.4 neq m^{-3} and 3.7 to 335.6 neq m^{-3} , respectively, and the variations of $_{\text{sam}}\text{SO}_4^{2-}$ and $_{\text{nss}}\text{SO}_4^{2-}$ concentrations decrease gradually and reach the minimum in 1999. Afterwards, they become greater the years of 2000 to 2003. This trend is similar to other long-term observations (Ito and Mizohata, 2006). There is no clear seasonal variation, although $_{\text{nss}}\text{SO}_4^{2-}$ concentrations are slightly high in summer.

The $_{\text{sam}}\delta^{34}\text{S}$ and $_{\text{nss}}\delta^{34}\text{S}$ in aerosols range from $+1.0$ to $+15.1$ with a mean value of $+5.7\text{‰}$, and from -4.4 to $+14.5$ with a mean value of $+4.1\text{‰}$, respectively. Variation ranges of $_{\text{sam}}\delta^{34}\text{S}$ and $_{\text{nss}}\delta^{34}\text{S}$ values abruptly narrowed after 2000. Kawamura *et al.* (2002) reported $_{\text{nss}}\delta^{34}\text{S}$ values of aerosols collected at Fukuoka, located in Kyushu Island, Japan, ranged from $+0.4$ to 4.9‰ during March 1999 to January 2000. These results are comparable to our results obtain in the same period.

To detect the seasonal variation, we plot seasonal mean $_{\text{sam}}\delta^{34}\text{S}$ and $_{\text{nss}}\delta^{34}\text{S}$ values with the variation range (spring, March–May; summer, June–August; fall, September–November; winter, December–February) in Fig. 4. The average values of $_{\text{sam}}\delta^{34}\text{S}$ and $_{\text{nss}}\delta^{34}\text{S}$ are slightly lower in summer and high in the other three seasons, in which they are almost at the same level. The $_{\text{sam}}\delta^{34}\text{S}$ values are lower than the values of sea salt sulfate ($+20.3\text{‰}$). The difference of $_{\text{sam}}\delta^{34}\text{S}$ and $_{\text{nss}}\delta^{34}\text{S}$ values in summer is smaller than in other three seasons, which indicates that contributions of sea-salt sulfate are low in summer (average: 3.5%) and high during the other seasons (average: 12.2%).

Source identification of sulfate in aerosols

The seasonal variations of $_{\text{nss}}\delta^{34}\text{S}$ values suggest that $_{\text{nss}}\text{SO}_4^{2-}$ in aerosols are derived from sources with lower $\delta^{34}\text{S}$ values in summer than in other seasons. Atmospheric sulfur compounds originate mainly from four natural and anthropogenic sources: industrial (anthropogenic) sulfur, bacteriogenic sulfur, sea spray sulfate, and volcanic sulfur. Regarding the cause of the high values of $_{\text{nss}}\delta^{34}\text{S}$ except summer, bacteriologic hydrogen sulfide and volcanic

Fig. 3. Seasonal variation of (a) atmospheric samSO_4^{2-} (●) and nssSO_4^{2-} (○) concentrations and (b) $\text{sam}\delta^{34}\text{S}$ (●) and $\text{nss}\delta^{34}\text{S}$ (○) values of aerosols collected at Tsuruoka, Japan in the period of 1993–2003.

sulfur are less likely sources, because bacterial activity occurs mainly in summer (Hatakeyama, 1985) with low $\delta^{34}\text{S}$ values (Nakai and Jensen, 1967), and there was no large-scale volcanic activity during the period of sampling, except for the Miyake-jima eruption in 2000 (Akata *et al.*, 2004). During fall to spring, northwesterly monsoons blow into Japan and carry air masses including many kinds of materials from the Asian continent. On the other hand, high-pressure systems develop in the Pacific Ocean in summer, and bring air masses to Japan from the ocean. Therefore, effect of the continental source will be small in summer. It seems that $\text{nss}\delta^{34}\text{S}$ values in summer are the background values of the sampling area (which has a mixture of local anthropogenic sulfur and local biogenic sulfur), and $\text{nss}\delta^{34}\text{S}$ values in other three seasons are composites of the background values and values of other origins.

China is located in the windward of the northwesterly monsoon. In China, many consecutive years of high economic growth in this period were accompanied by increasing energy demands, greater coal combustion, and even greater emissions of pollutants (Fu *et al.*, 2007). Therefore, gases and aerosols (fly ash) discharged by fossil fuel combustion have created serious environmental problems. The main fossil fuel used in China is coal, and anthropogenic SO_4^{2-} aerosols in the atmosphere are mainly produced by oxidation of SO_2 emitted by coal combustion.

Fig. 4. Maximum and minimum values (■), mean values and ranges of $\text{sam}\delta^{34}\text{S}$ (▲) and $\text{nss}\delta^{34}\text{S}$ (●) in aerosols during the four seasons at Tsuruoka, Japan (error bars show S.D.).

To identify the sources of $\text{nss}\delta^{34}\text{S}$ in wet deposition, which is high in winter, Ohizumi *et al.* (1997) investigated the $\delta^{34}\text{S}$ in wet deposition and fossil fuels. They found that the $\delta^{34}\text{S}$ values of wet deposition in Niigata in winter were in agreement with the $\delta^{34}\text{S}$ values of coal used in China

(greater than +6.0‰). The SO_4^{2-} aerosols produced by homogenous and heterogeneous oxidation reactions are enriched in heavier sulfur isotopes than atmospheric SO_2 (Saltzman *et al.*, 1983; Mukai *et al.*, 2001). Kawamura *et al.* (2002) suggested that there was a strong possibility of long-range transport of SO_4^{2-} from continental Asia to the southern Japanese island of Kyushu, because the high $\delta^{34}\text{S}_{\text{nss}}$ values in winter bulk precipitation could not be explained only by the isotopic fractionation effect of these oxidation reactions in a fluid layer on the aerosol surface. The main fossil fuel used in Japan is petroleum imported mainly from the Middle East countries. Ohizumi *et al.* (1997) reported $\delta^{34}\text{S}$ values of petroleum used in Japan ranged from -8.2‰ to $+7.2\text{‰}$ with a mean value of -3.3‰ . Maruyama *et al.* (2000) also reported they ranged from -6.8‰ to $+9.1\text{‰}$ with mean value of -0.64‰ . Therefore, the contribution of sulfur compounds produced by petroleum combustion in Japan is thought to be small. During the coal combustion process in industrial and domestic uses of coal as fuel, released gaseous sulfur compounds such as SO_2 are invariably enriched in lighter sulfur isotopes relative to the corresponding coal. In contrast, particles such as fly ash are always rich in heavier sulfur isotopes (Hong *et al.*, 1993). The $\delta^{34}\text{S}_{\text{nss}}$ in aerosols in fall to spring are close to the average $\delta^{34}\text{S}$ values of coal used in northern China which range from 0 to $+15\text{‰}$ with a mean value of $+7.4 \pm 8.8\text{‰}$ (Motoyama *et al.*, 2002). These results indicate that the long-range transport of sulfate from the Asian continent to Japan might be the source of the high $\delta^{34}\text{S}_{\text{nss}}$ values in fall to spring.

On the other hand, sulfate salts are included in the source materials of Asian dust and are therefore inferred to contribute to long-range transport of those components. Yabuki *et al.* (1999) reported that $\delta^{34}\text{S}$ values of salt materials collected in the Xinjiang Province varied widely, -30.3 to $+26.1\text{‰}$, with the most frequently occurring values of $+5$ and $+10\text{‰}$. Yanagisawa *et al.* (1997) also reported $\delta^{34}\text{S}$ values of $+5$ to $+18\text{‰}$ for desert sand and loess collected in the Taklimakan Desert and Loess Plateau. These values are higher than those of sulfate in aerosols. The relationship between the $\delta^{34}\text{S}_{\text{nss}}$ in aerosols and those in desert sand and loess remains unclear. High $\delta^{34}\text{S}$ values sometimes appear during spring and fall. Therefore, one of the sources of SO_4^{2-} in atmospheric aerosols in spring and fall could be desert sand and loess SO_4^{2-} transported from the arid and semi-arid regions of China.

Change of the trend of SO_4^{2-} concentration and $\delta^{34}\text{S}$ values

As mentioned before, the trend of SO_4^{2-} and $\delta^{34}\text{S}_{\text{nss}}$ concentrations reaches the minimum in 1999. To prevent the increase in anthropogenic emissions of pollutants and consumption of coal, China enacted the “Air Pollution Control Act” for environmental protection in

Fig. 5. Non-sea salt sulfate concentrations versus $\delta^{34}\text{S}_{\text{nss}}$ in aerosol samples collected at Tsuruoka, Japan in the period of 1993–2003.

1978. This act was revised to provide better air quality protection in 1995 (Study Group on China Environmental Problem, 2004). The energy structure changed from coal to petroleum and clean fuels (nuclear energy and hydroelectricity) (Fang *et al.*, 2009) with application of pollution control technologies to plants. As a result, among the fuel consumptions, only the amount of coal has decreased since 1997 with the minimum in 2000 (Akimoto *et al.*, 2006). The SO_2 emission in China slightly decreased from 1995 to 2002 (Ohara *et al.*, 2007). On the other hand, the numbers of motor vehicles in China have been rapidly increasing since 1990 (Liu and Diamond, 2005). Carmichael *et al.* (2002) suggested that the decline of SO_2 emissions in China was due to a reduction in industrial coal use, a slowdown of the Chinese economy, and the closure of small and inefficient plants among other reasons. Therefore, the changes in energy structure in China would have caused the decreasing trend of SO_4^{2-} concentration in aerosols transported from China to Tsuruoka.

The variation ranges of $\delta^{34}\text{S}_{\text{sam}}$ and $\delta^{34}\text{S}_{\text{nss}}$ values abruptly changed after 2000. Relationships between SO_4^{2-} concentrations and $\delta^{34}\text{S}_{\text{nss}}$ in aerosols are shown in Fig. 5. The $\delta^{34}\text{S}_{\text{nss}}$ values converge to around 0 to 5‰ with increasing in SO_4^{2-} concentration. Almost all $\delta^{34}\text{S}_{\text{nss}}$ values in summer are around 0 to $+5\text{‰}$ (Fig. 4), and SO_4^{2-} concentrations are slightly higher in summer than other three seasons. It means that they probably originated from local sulfur sources. We can interpret Fig. 5 as showing the mixing of sulfur sources (local sulfur with 0 to $+5\text{‰}$, continental sulfur with high $\delta^{34}\text{S}$ values and other sulfur with low $\delta^{34}\text{S}$ values). In China, besides

the changes in energy structure mentioned above, environmental protection regulations are being revised steadily since 1995, and Chinese economic growth is gradually being controlled by stronger policies. To control sulfur emissions, China has introduced the technologies for improving combustion efficiency and fuel gas desulfurization (FGD) technologies for removal of TSP and SO₂. Zhang (2005) reported that FGD technologies (wet-based) were introduced to industrial plants of coke production and thermal power station since 1998 at Shanxi Province, from which the air-mass flows into Yamagata prefecture during fall to spring, and that over 40% of the plants had accepted the technologies by 2001. These technologies can enrich the lighter sulfur isotopes into released SO₂ (Derda *et al.*, 2007), which would have caused the abrupt change in the variation ranges of $\delta^{34}\text{S}_{\text{sam}}$ and $\delta^{34}\text{S}_{\text{nss}}$ values after 2000.

CONCLUSIONS

Aerosol samples were collected in an area of Japan on the Sea of Japan during 10 years. Concentrations of water-soluble chemical components and sulfur isotopic ratios of sulfate in the samples were measured to evaluate their temporal variations and identify the sulfate source.

(1) The SO_4^{2-} and SO_4^{2-} concentrations range from 7.6 to 354.4 and 3.7 to 335.6 neq m⁻³, respectively, and show no clear seasonal variation.

(2) Sulfur isotope ratios of sulfate ($\delta^{34}\text{S}_{\text{sam}}$) and non-sea salt sulfate ($\delta^{34}\text{S}_{\text{nss}}$) in aerosols range from +1.0 to +15.1 with a mean value of +5.7‰ and -4.4 to +14.5 with a mean value of +4.1‰, respectively.

(3) The values of $\delta^{34}\text{S}_{\text{sam}}$ and $\delta^{34}\text{S}_{\text{nss}}$ are relatively low in summer and high in the other three seasons, suggesting that SO_4^{2-} in aerosols was derived from sources with lower $\delta^{34}\text{S}$ values in summer than in the other three seasons. The most important source of sulfur compounds in aerosols in fall to spring is anthropogenic sulfur produced by fossil fuel combustion on the Asian continent.

(4) The SO_4^{2-} concentrations in aerosols decrease gradually and reach the minimum in 1999, which would be caused by the decline of SO₂ emissions in China due to a reduction in industrial coal use, a slowdown of the Chinese economy, and the closure of small and inefficient plants among other reasons.

(5) The variation ranges of $\delta^{34}\text{S}_{\text{sam}}$ and $\delta^{34}\text{S}_{\text{nss}}$ values abruptly changed after 2000. The introduction of flue gas desulfurization (FGD) technologies to industrial plants of coke production would be one of the most important causes of this change.

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