Note

Combination of Sulfur Isotope Ratio of Non-sea Salt Sulfate and Lead-210 Concentration in Aerosols as an Index of Long-range Transported Aerosols

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We studied on the validity of combination of ^{210}Pb concentration and sulfur isotope ratio of non-sea salt sulfate in aerosols as an index of long-range transported aerosols. As a result, it was found that multi-isotope method using ^{210}Pb and $\delta^{34}\text{S}$ was useful for long-range transported aerosols from the Asian continent.

Key Words : sulfur isotope ratio, lead-210, aerosol, Asian dust

1. Introduction

In the Asian dust (Kosa) events, continental surface soil particles (from the arid and/or semi-arid region in China and Mongolia) are blown into the upper atmosphere and transported aloft by strong westerly winds; the dust is often observed over Japan in spring and fall seasons. Asian dust has been attracting attention in many fields because of its significant influences on both the local and global environments¹⁾. In addition, various pollutants are also brought from the Asian continent to Japanese Archipelago²⁾ as gaseous materials and/or sub-micron aerosols to which they attach. Many re-

searchers have studied on characteristics and influence of long-range transported chemical substances^{2)–5)}. Therefore, it is important to understand the source and properties of Asian dust aerosols.

Radioisotopes (for example: ^{210}Pb and ^{137}Cs) and isotope ratios (for example: $\delta^{34}\text{S}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) are often used as tracers for evaluating the source of aerosols^{6)–9)}. Lead-210 (^{210}Pb) is a natural radionuclide in the ^{238}U decay series with relatively long half-life ($T_{1/2}$ of 22.3 y). Airborne ^{210}Pb is produced from its precursor, ^{222}Rn ($T_{1/2}$ of 3.82 d), emanated from the ground surface. The ^{210}Pb attaches to aerosol particles near the ground surface, and is trans-

ported through the atmosphere¹⁰⁾. On the other hands, it is well-known that the atmospheric sulfur has natural and anthropogenic origins. The source of anthropogenic sulfur is mainly fossil fuel combustion. Recently, Chinese economic development is remarkable, and the emission rate of the anthropogenic sulfur is increasing. The anthropogenic sulfur has been carried as Asian dust particles (gypsum and attached particles). Therefore, in Japan, it is suggested that source of sulfur and ^{210}Pb are East Asian Region in fall to spring^{9), 11)}.

We have observed atmospheric aerosols in Tsuruoka City, Yamagata Prefecture since 1993, and reported the chemical composition¹²⁾. In addition, we also reported sulfur isotope ratio of non-sea salt sulfate ($_{\text{nss}}\delta^{34}\text{S}$) and ^{210}Pb in aerosols in the same period^{13), 14)} to clarify the characteristics of long-range transported aerosol particles. However, the relationship between $_{\text{nss}}\delta^{34}\text{S}$ and ^{210}Pb in aerosols has not yet been studied. If $_{\text{nss}}\delta^{34}\text{S}$ and ^{210}Pb show a good correlation, their combination may be considered as a reliable indicator. In this paper, we reported the relationship between $\delta^{34}\text{S}$ of sulfate and ^{210}Pb in aerosols to evaluate them as an indicator of long-range transported aerosols from East Asian continent (Asian dust and pollutants).

2. Experimental

The sampling method is identical to that we used previously¹³⁾. The analytical procedures and results of $\delta^{34}\text{S}$, ^{210}Pb and major chemical components has also been reported elsewhere^{13), 14)}. Briefly speaking, the sampling site is the building top of Tsuruoka National College of Engineering Technology in Tsuruoka, Yamagata Prefecture, Japan ($38^{\circ}42'\text{N}$, $139^{\circ}47'\text{E}$, approximately 9 km away from the seashore

Fig. 1 Location map of sampling site (Tsuruoka City)

of the Sea of Japan and 20 m high above the ground level), shown in Fig. 1. The aerosol samples were collected for about 5 days using a high-volume air sampler (HVC-1000, Shibata) with a quartz-fiber filter ($20.3\text{ cm} \times 25.4\text{ cm}$, QR-100, Advantec) and/or PTFE filter (PF040, Advantec, Japan) during 1996 to 1999. The air-flow rate was approximately 700 L min^{-1} .

The filters with collected aerosols were cut into quarters and the extraction with water was carried out by ultrasonic-wave. After filtration, Na^+ and SO_4^{2-} concentrations were measured by ICP-AES (SPS7000A, Seiko) and Ion chromatography (2020i, Dionex), respectively. After chemical analysis, 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 $\text{SiO}_2\text{-V}_2\text{O}_5$ in a vacuum line¹⁵⁾. Subsequently, $\delta^{34}\text{S}$ was measured using a stable isotope ratio mass spectrometer (Delta-E, Finigan-MAT). The results of $\delta^{34}\text{S}$ is reported in Canyon Diablo Troilite (CDT) scale, which is de-

fined as

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

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 pre-processing operation is better than $\pm 0.2\%$.

The ^{210}Pb in aerosols were analyzed by a γ -ray spectrometer with a well-type Ge semiconductor detector using 1/16 dried filters¹⁶⁾.

On the basis of Na^+ as the tracer for sea salt component, non-sea salt SO_4^{2-} (nssSO_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:

$$\begin{aligned} \text{nssSO}_4^{2-} &= \text{samSO}_4^{2-} - \frac{\text{seaSO}_4^{2-}}{\text{seaNa}^+} \times \text{samNa}^+ \quad (2) \\ \text{nss}\delta^{34}\text{S} &= \frac{[\text{sam}\delta^{34}\text{S} \times \text{samSO}_4^{2-} - \text{sea}\delta^{34}\text{S} \times (\text{samSO}_4^{2-} - \text{nssSO}_4^{2-})]}{\text{nssSO}_4^{2-}} \quad (3) \end{aligned}$$

where samSO_4^{2-} and samNa^+ are SO_4^{2-} and Na^+ concentrations in each samples, seaSO_4^{2-} and seaNa^+ are SO_4^{2-} and Na^+ concentrations in seawater, and $\text{sam}\delta^{34}\text{S}$ and $\text{sea}\delta^{34}\text{S}$ are $\delta^{34}\text{S}$ values of sample and seawater ($+20.3\%$), respectively.

3. Results and discussion

Monthly variations of (a) SO_4^{2-} and nssSO_4^{2-} concentrations, (b) $\delta^{34}\text{S}$ and $\text{nss}\delta^{34}\text{S}$, and (c) ^{210}Pb concentration in aerosols are shown in Fig. 2 (January 1996 – May 1999). Atmospheric concentration of SO_4^{2-} and nssSO_4^{2-} ranged from 0.99 to 10.32 and from 0.95 to 10.21 $\mu\text{g m}^{-3}$, respectively. They are in good correlation. And $\delta^{34}\text{S}$ and $\text{nss}\delta^{34}\text{S}$ ranged from 0.97 to 14.90 and from 0.76 to 13.87‰, respectively. Although

Fig. 2 Variation of (a) atmospheric concentration of SO_4^{2-} and nssSO_4^{2-} , (b) sulfur isotope ratio of sulfate ($\delta^{34}\text{S}$) and non-sea salt sulfate ($\text{nss}\delta^{34}\text{S}$) and (c) atmospheric concentration of ^{210}Pb at Tsuruoka, Japan

$\delta^{34}\text{S}$ and $\text{nss}\delta^{34}\text{S}$ were slightly low in summer, clear seasonal variation was not recognized in the atmospheric concentration of SO_4^{2-} (nssSO_4^{2-}) and $\delta^{34}\text{S}$ ($\text{nss}\delta^{34}\text{S}$) because of lack of data. The ^{210}Pb concentration ranged from 0.3 to 3.4 mBq m^{-3} and became low in summer and relatively high in other seasons, showing a seasonal variation.

Figure 3 shows the relationships between atmospheric concentration of ^{210}Pb and nssSO_4^{2-} . It is a good correlation ($r=0.45$, $p<0.05$). It is known that the sulfate aerosols are generated from gaseous sulfur (mainly SO_2)¹⁷⁾. However, Yanagisawa et al.¹²⁾ reported that SO_2 concentration is constant in this area through the year. So, variation of sulfate concentration would mean the presence of the additional sulfate aerosols. In Tsuruoka, north western monsoon

Fig. 3 Relationship between atmospheric concentration of ^{210}Pb and atmospheric concentration of non-sea salt sulfate at Tsuruoka

Fig. 4 Relationship between atmospheric concentration of ^{210}Pb and sulfur isotope ratio of non-sea salt sulfate in aerosols at Tsuruoka

is dominant in fall to spring. Therefore, the source of atmospheric ^{210}Pb and nssSO_4^{2-} in fall to spring seasons is supposed to be mainly East Asian continent.

Figure 4 shows the relationships between atmospheric ^{210}Pb concentration and sulfur isotope ratio of non-sea salt sulfate in aerosols at Tsuruoka. It shows a weak positive correlation ($r=0.28$). It is reported that atmospheric nssSO_4^{2-} and ^{210}Pb concentrations are increased by continental air-mass. As the origin of sulfur aerosols, two sources are considered. The one is the continental surface soil particles in arid and semi-arid region including sulfur compounds and the other is secondary aerosols produced by anthropogenic sulfur components. They would be mixed in the atmosphere. Their isotope ratios have wide range values depending on regions. Ito et al.¹⁸⁾ reported that $\delta^{34}\text{S}$ in sand and loess ranged from -0.66 to $+29.50\text{‰}$ (Ave. $\pm$ S.D.: $+11.63 \pm 6.70\text{‰}$), and $\delta^{34}\text{S}$ values were high in Loess Plateau area and low in Taklimakan Desert area. In addition, Motoyama et al.¹⁹⁾ summarized that $\delta^{34}\text{S}$ values in coals in East Asian area ranged from -27.3 to $+28.9\text{‰}$ with a mean value of $+4.2 \pm 9.6\text{‰}$, and

those values in northern China (north of 40°N) were higher than southern China (south of 40°N). Two high data of sulfur isotope ratio in Fig. 4 were observed in November and December. These results indicate that the nssSO_4^{2-} in aerosols in fall to spring were mainly derived from source regions including high $\delta^{34}\text{S}$ source such as fossil fuel combustion in north of China and desert sand (loess). Therefore, it seems that the atmospheric aerosols in Tsuruoka were mainly transported from the northern China when ^{210}Pb concentration and $\text{nss}\delta^{34}\text{S}$ showed high values in the same period. Especially, high sulfur isotope ratio suggests much contribution of anthropogenic origin. It is concluded that multi-isotope method using ^{210}Pb and $\delta^{34}\text{S}$ is a useful index for evaluating the source of long-range transported aerosols.

4. Conclusions

We studied on the validity of combination of ^{210}Pb concentration and $\text{nss}\delta^{34}\text{S}$ in aerosols as an index of long-range transported aerosols. As a result, it was suggested that multi-isotope method using $\delta^{34}\text{S}$ and ^{210}Pb was useful. As mentioned before, previous studies have re-

ported the validity of Sr-Nd isotopes, stable Pb isotopes and $^{137}\text{Cs}/^{90}\text{Sr}$ ratio as tracers of aerosols. The multi-isotope method combined with many other isotopes will be necessary for evaluating exact source region of transported aerosols in future study.

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要 旨

硫黄同位体比と ^{210}Pb 濃度を用いた大陸起源エアロゾルの検討

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大気エアロゾルの供給源を明らかにする手法の一つとして、大陸起源エアロゾルの指標として利用されてきた大気中 ^{210}Pb 濃度と非海塩性硫酸イオンの硫黄同位体比 ($_{\text{nss}}\delta^{34}\text{S}$) を組み合わせて利用することを試みた。その結果、両者には正の相関が認められ、両者を組み合わせた方が、より大陸起源エアロゾルの指標として有効であった。