제주에서 $^{207}Pb/^{206}Pb$과 $^{208}Pb/^{206}Pb$를 이용한 에어로졸 중의 Pb 오염원 규명

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Source identification of Pb in aerosols at Jeju-do, Korea by using $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$

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국 문 요 약

2002년 4월에 제주도 북부지역에서 에어로졸과 소각장의 비산재, 자동차 배기가스, 토양 등의 오염물질들을 채취하여, 에어로졸에서 Pb 오염원을 규명하기 위해 시료의 Pb ratio($^{207}Pb/^{206}Pb$와 $^{208}Pb/^{206}Pb$)를 분석하였다. 시료의 전처리는 초음파로 하였고, Pb ratio는 ICP-MS를 이용해 측정하였다. 에어로졸의 Pb ratio는 시료 채취일별로 두 개의 그룹으로 분류하였다.

하나의 그룹은 지역 오염원들이 에어로졸에 매우 크게 기여한다고 사료되는 오염원들과 관련된 오염원에서는 유사한 Pb ratio를 보였다. 다른 한 그룹은 지역 오염원들로부터 다른 Pb ratio를 보였고, 처음 그룹의 Pb ratio와 비교하여 비교적 높은 Pb ratio를 보였다. 이러한 연구 결과는 아시아 대륙에서 북서계절풍에 의해 이동된 사막 모래에서 높은 비율을 가진 Pb의 장거리 수송 때문으로 사료된다.

Key words : 에어로졸, Pb ratio($^{207}Pb/^{206}Pb$와 $^{208}Pb/^{206}Pb$), 북서계절풍, 장거리 수송.

1. Introduction

The long range transport of air pollutants from continental Asia to Japan is of great concern.[1,2] The air pollutants are classified into two kinds of materials. One kind are anthropogenic products caused by the combustion of large amounts of fossil fuels, such as SO_2, NOx and their oxidants. In continental Asia, these products have increasing concurrent with the amount of fossil fuel consumption, due to rapid population growth.[3] The other kind of pollutant is a natural product, such as Kosa (the Japanese name), which consists of sand coming from the Asian desert to Japan. Recently, Kosa has been frequently observed throughout Japan during the spring season. In the costal areas of the Sea of Japan, increments of sulfur deposition have been reported by numerous investigators.[4-6] The increments have been attributed to the long range transport of air pollutants, such as sulfate caused by fossil fuel combustion, and Kosa, from continental Asia to Japan by northwest seasonal winds.[7-11] Since it is expected that the amounts of air pollutants transported from continental Asia to Japan will increase in the future, source identification will be very important for estimating the amounts of pollutants released from the various sources.

Pb has four stable isotopes. three of these isotopes, ^{206}Pb, ^{207}Pb, and ^{208}Pb are formed at different rates the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, respectively. The fourth isotope, ^{204}Pb, has no radioactive progenitor. Therefore, the isotopic composition of a Pb ore is dependent on the original Pb, U, and th concentrations, and by its deposit age. Similarly, Pb in various non-ore materials, such as coal and surface soil, also has a particular isotopic composition due to U and Th

contained as trace elements. Pb released into the atmosphere by combustion, smelting, and other processes retains the isotopic composition of original sources, because normal chemical and physical processes do not affect Pb isotopic composition. Therefore, we can estimate the sources of Pb in aerosols by examining the differences in the isotopic composition. Sturges et al. reported that the Pb ratio ($^{206}Pb/^{207}Pb$) in aerosols in the United States were differentfrom those in Canada, concluding that the difference was attributable to the sources of Pb additives for gasoline in each country.[12]

Mukai et al. evaluated the current Pb pollution in the urban atmosphere of Asian countries using Pb ratios ($^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$), and confirmed the regional sources of Pb.[13]

In this investigation, we measured the Pb ratios of aerosols collected at Jeju-do, Korea, and discuss here the long range transport of the air pollutants.

2. Experimental

2.1 Samples

Jeju-do is the coasts of Korea and is about 100km south of the Korean Peninsula, at about 300km west Kyushu Island, Japan, as shown in **Figure 1**. It is not developed and possesses abundant natural beauty, and there are no chemical or industrial plants operating. Therefore, Jeju-do is a suitable site for monitoring the air pollutants transported from continental Asia.

Aerosol samples were collected on a membrane filter (A300A, pore size 3 μm, 110mm dia., Advantech, Japan) using a low-volume air sampler (HVS-500, Shibata Scientific Tech. Ltd.) with a flow rate of 300 L/min over a period from 3 to 4 hours. Two sampling sites (City "Hall and Cheju National University) were selected, both of which are located at the northeastern part of Jeju-do. The samples were taken on the roofs of the buildings. the aerosol samplings were carried out from April 8th to 17th.

In addition to the aerosol samples, source related materials were also collected, and Pb ratios were measured for comparison. the details about the samples are summarized below. The samples consisted of the following : (1) Fly ash from house-use refuse incinerators used around the downtown area. (2) Vehicle exhaust particulates (soot samples which adhered to exhaust pipes were collected as vehicle exhaust pipes were collected as vehicle exhaust particulates). (3) Surface soil samples.

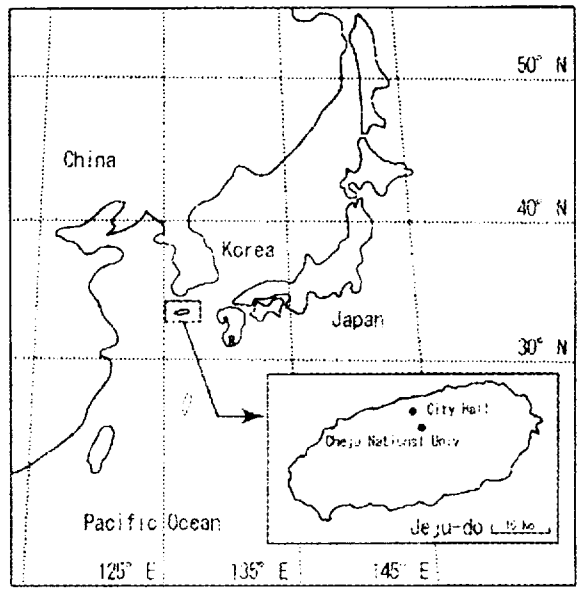

Fig. 1. Sampling sites for collecting aerosols.

2.2. Pretreatment and measurement

Microwave digestion was applied as the sample pretreatment. This method causes minimal Pb contamination and can digest the sample quickly and completely. The digestion was carried out according to the method by Kawamura et al.[14] The aerosol samples were put in an inner microwave vessel (DV-15, San-ai Kagaku Co., Ltd) directly together with the membrane filter. For the source related materials, about 50mg of the sample was put in the vessel. Two mL of 60% HNO_3 (Merck ultrapure grade) and 0.5mL of 48% HF (Merck ultrapure grade) solutions were added. The inner vessel was set into

an outer microwave digestion vessel (PT-70, San-ai Kagaku Co., Ltd.) containing 1mL of distilled water. The outer vessel was set in a jacket (PP-70, San-ai Kagaku Co., Ltd.). the jacket was placed on a turntable in an ordinary microwave oven, and the sample was digested by microwave (5min × 3 times). The digested sample was evaporated to near dryness on a hotplate. The residue was dissolved in about 10mL of 1M HNO_3 and filtrated with a cellulose filter (5C, Advantech). Finally, the Pb concentration in the sample solution was adjusted to about 20 μg/L with 1M HNO_3. After adjustment of the Pb concentration, the sample solution was subjected to determination of the Pb ratios by ICP-MS. A blank sample was also prepared in the same manner.

The Pb ratios were determined with a quadrupole mass spectrometer ICP-MS (Model 4500, Hewlett Packard). In this investigation, ^{206}Pb, ^{207}Pb, and ^{208}Pb were measured. A blank sample was also measured, and the ion counting rate of each isotope was subtracted from that of the sample. The observed ratios of $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ were calculated using the net ion counting rate of each isotope.The reference material NIST SRM 981 was used to determine the normalization factors for correction of the mass discrimination effect. The normalization factor is defined as the ratio of the observed lead isotope ratio to the certified value of SRM 981. In this investigation, the observed isotope ratios were divided by the normalization factor to determine the final Pb ratios.

3. Resuls and Discussion

Pb ratios of the aerosols at Jeju-do are shown in **Figure 2**. The Pb ratios of $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ranged from 0.864 to 0.878, and from 2.110 to 2.147, respectively. the Pb ratios were widely variable, and were roughly classified into two groups, depending on the sampling date. One group (group-Ⅰ) consisted of the Pb ratios collected on April 16th, and the other group(group-Ⅱ) consisted of those collected on April 8th, 9th, 10th and 17th. The latter Pb ratios of $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ were clearly higher than the former ones, suggested that there were at least two primary Pb sources of the aerosols during the sampling periods, and that the degree of their contribution to the aerosols varied from day to day.

It is known that the Pb ratios of aerosols differ considerably among countries, and these differences correspond to differences in the regional sources of pb.[13] In Korea, the Pb ratios of $^{207}Pb/^{206}Pb$ of aerosols collected at Seoul were reported to range from 0.848 to 0.877 by Mukai et al., and from 0.84 to 0.87 by Lee and Lee.[13, 15] Their data were about the same as the data collected in thus study, and large variation of Pb ratios were observed not only in Seoul, but also in Jeju-do Mukai et al. pointed out that there seems to be relatively large local sources in Korea, such as leaded gasoline, coal used as an energy local source in Korea, such as leaded gasoline, coal used as an energy source, and Pb ore (and related materials), and their contributions may change with meteorological conditions and with the seasons.[13]

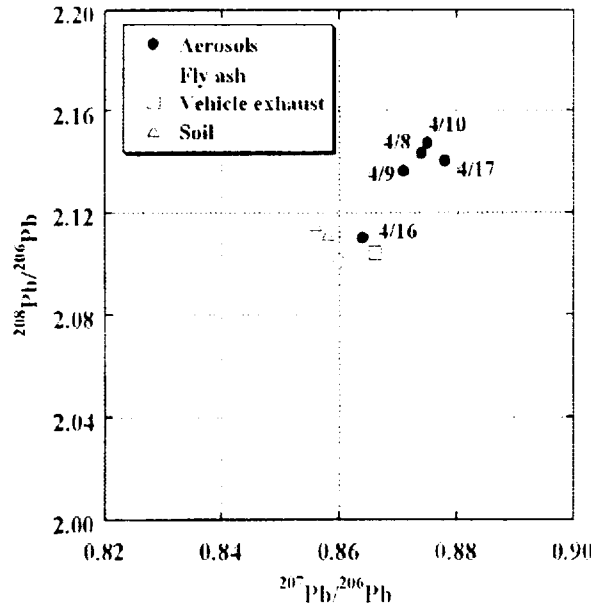

Fig. 2. Pb ratios of aerosols and sources related materials at Jeju-do, Korea.

The Pb ratios of the source related materials at Jeju-do are shown in **Figure 2** along with those of the aerosols. The variability of the Pb ratios of the sources selected in this investigation were relatively small, despite the fact that the Pb ratios of sources in Korea were believed to be quite variable. The Pb ratios of the aerosols collected on April 16th(group-Ⅰ) were similar to those of the sources, especially fly ash from incinerators or vehicle exhaust, suggesting that there was a large contribution of regional sources to the aerosols collected on this day. However, the Pb ratios on other days(group-Ⅱ) differed from those of those of the regional sources, and were relatively high. This indicates that there were other sources with high Pb ratios.

In the spring season from march to April, Kosa has been observed at Jeju-do every year. according to the Jeju Institute of Public Health & Environmental Research, Kosa has been identified by examining several factors, such as meteorological conditions, satellite photographs, and PM10 concentrations. During the periods of this investigation, the PM10 concentrations measured by the Jeju institute changed largely from day to day, as shown in Figure 3, and Kosa was identified on April 8th, 9th, 10th, 13th, 14th and 17th on the basis of those factors. These dates are in good agreement with the sampling dates on with the Pb ratios of the aerosols showed high values(group-Ⅱ). Therefore, Kosa was considered to be one of the primary sources of Pb in this investigation.

Kosa is well known to originate in the areas of the Gobi desert, the Taklamakan desert, abd the dry (semi-arid) regions of continental Asis. Quan et al. reported the size distributions of Pb ratios for five kinds of desert sands (Lanzhou, Tenger, Zhangye, badanjilin and Wulmuqi) in the northwest of china.[16]

The Pb ratios of $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ranged from 0.8287 to 0.8674 and from 2.0560 to 2.1006, respectively. These data do not correspond to the Pb ratios of the aerosols (group-Ⅱ), and clearly show low values. Therefore, there seem to be other reasons for the high ratios of aerosols.

Two reasons have been considered for the high Pb ratios of the aerosols(group-Ⅱ) and mentioned below. (1) there have been few papers on the Pb ratios of desert sands in continental Asia. It is still uncertain whether the Pb ratios of desert sands previously reported by Quan et al. are representative of all the desert areas in continental Asia, because the data was not comprehensive. (2) There is a large possibility that Pb with high Pb ratios are transported together with Kosa by northwest seasonal winds. For example, Pb ores from the Korean Peninsula were reported to have relatively high Pb ratios.[17]

Pb isotope ratios were useful for identifying the sources of Pb in aerosol. However, the number of samples studied in the present study was insufficient to adequately discuss the variation of Pb ratios of aerosols, and the relationship of these aerosols to Pb sources. Therefore, further research is needed to clearly explain the long range transport of air pollutants.

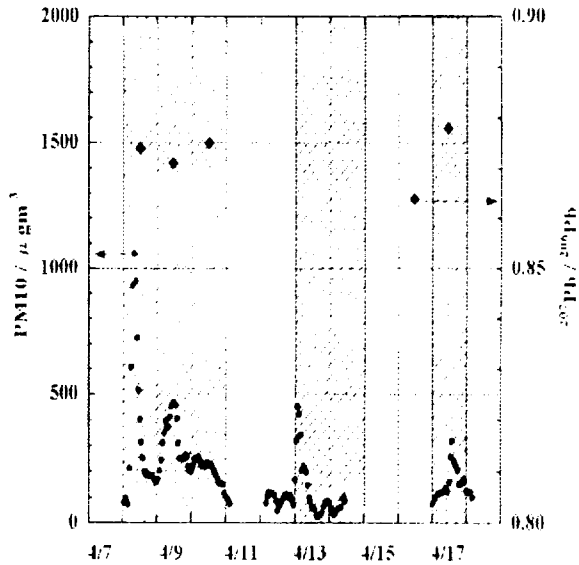

Fig. 3. Daily varations of pb ratios and PM10 comcentrations at jeju-do, Korea. the days that Kosa was observed were showed by shaded areas.

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References

1. S. Fujita, Kankyo Kagaku Kaishi 9. 185 (1996).
2. G. Mastsumoto, A. Utsunomiya and O. Oishi, J. Jpn. Soc. atmos. Environ. 34, 1(1999).
3. S. Hamedd and J. Dignon, J. air Waste Manage Assoc. 42, 159 (1992).
4. T. Ohizumi, N. Fukuzaki, N. Moriyama, Y. Urushiyama and M. Kusakabe, Nippon Kagaku Kaishi 1991, 675 (1991).
5. M. Kitamura, M. Sugiyama, T. Ohhashi and N. Nakai, Chikyu kagaku (Geochemistry)27, 109(1993).
6. T. Ohizumi, N. Fukuzaki and M. Kusakabe, Nippon kagaku kaishi 1994, 882(1994).
7. T. Ohizumi, N. Fukuzaki and M. Kusakabe, Atmos. Environ. 31, 1339(1997).
8. R. Motoyama, F. Yanangisawa, A. kawabata and A. Ueda, Seppyo 62, 215(2000).
9. F. Yanangisawa, N. Akata, R. Motoyama, A. kawabata and A. Ueda, J. Ecotechnology Res. 7, 1 (2001).
10. H. Kawamura, N. Matsuoka, S. Tawaki and N. Momoshima, Water, Air, and Sil Pollu. 130, 1775(2001).
11. H. Kawamura, S. Tawaki, N. Matsuoka, T. Nagano, N. Momoshima, S Osaki and Y. maeda, Chikyukagaku36, 23(2002).
12. W. T. Sturges and L. A. Barrie, Atmos. Environ. 23, 1645(1989).
13. H. Mukai, N. Furuta, T. Fujii, Y. Ambe, K. Sakamoto and Y. Hashimoto, Environ. Sci. Technol. 27, 1347 (1993).
14. H. Kawamura, H. Tagomori, N. matsuoka, Y. Takashima, S. Tawaki and N. Momoshima, J. Radioanal. Nuci. Chem. 242, 717(1999).
15. Y. Lee and D. Lee, Proceedings of the 2nd IUAPPA regional Conference on air pollution(Korea Air Pollution Research Assoc.: Seoul, Korea, 1991), p.121.
16. H. Quan, Y. Huang, M. Nishikawa and m. Morita, J. Environ. Chem. 4, 863(1994).
17. A. Sasaki, Kouzan Chishistu 37, 223(1987).