Distribution of stable isotopes of particulate lead in the atmosphere in Osaka, Japan

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Abstract

Poorly soluble particulate materials (PMs) in the atmosphere were collected in Osaka, Japan, over nine months, and the distribution of stable isotopes of lead in PMs was observed for elucidation of original sources of PMs. PMs were divided into three groups depending on their particle sizes, PM-1 (>10 μm), PM-2 (10 - 2.5μm), and PM-3 (<2.5μm). There were no differences in lead concentration among the three groups. Lead isotope ratios of total PMs during nine months were 0.880 $\pm$ 0.011 for $^{207/206}$ Pb, 2.137 $\pm$ 0.033 for $^{208/206}$ Pb, and 0.413 $\pm$ 0.007 for $^{207/208}$ Pb. There was no relationship between $^{208/206}$ Pb and $^{207/206}$ Pb in PM-2 and PM-3, although there was a significant relationship between both ratios in PM-1. Ratios of both $^{207/206}$ Pb and $^{208/206}$ Pb in PM-1 and PM-2 remained similar in each month, but both ratios in PM-3 dramatically raised and fell during nine months. From the present study, there may be various sources of lead PMs in the atmosphere, and the lead source of PM-3 may be different from PM-1 and PM-2.

Keywords: Lead; Stable isotope ratio; Particulate; Particle size; Atmosphere; Environmental pollution

1 Introduction

In the twentieth century, as leaded gasoline was one of the typical sources of environmental pollution, advanced countries gradually stopped using leaded gasoline (Weiss et al., 1999). Use of leaded regular gasoline stopped in 1978 in Japan (Hirao et al., 1986; Mukai et al., 1993). In contrast, China has been using leaded gasoline until recently, although it was banned in 1997 in large city areas (Chen et al., 2004; Wong and Li, 2004; Zheng et al., 2004). However, as lead is contained in, and contaminates, soil, trees, and many types of ores, the lead persists in the environment depending on economic development. For that reason, lead remains one of the sources of air pollution still now.

Lead has four stable isotopes; ^{204} Pb, ^{206} Pb, ^{207} Pb, and ^{208} Pb. ^{204} Pb does not decay, while ^{206} Pb decays from ^{238} U, ^{207} Pb from ^{235} U, and ^{208} Pb from ^{232} Th. The ratio of lead isotopes differs from each mine and ore source (Rabinowitz, 1995). Accordingly, the ratio is used to determine the original mine

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of any ore sample in geochemistry. In addition, the ratio is used to speculate on the original mine of ancient bronze in archeology. The ratio is also used for evaluation of lead in environmental pollution, using tree rings, sediment, clay, and biological specimens such as human urine and plasma (Gulson et al., 1995; Gwiazda and Smith, 2000; Scheuhammer et al., 2003). Especially, historical lead contamination has been observed from lead isotopes in sediments, tree rings, and so on (Weiss et al., 1999; Arnaud et al., 2004; Bindler et al., 2004). Gulson et al. (1995) observed that the ratio of $^{206/204}$ Pb in blood differed between people of mainland Australia and migrant women, because it is well known that the ratio of lead isotopes in Australian ores are significantly different from that in European ores. And there are several reports using lead isotopes in biological materials like urine and blood to evaluate household environments and environmental pollution (Gwiazda and Smith, 2000; Gulson et al., 2000).

Recently, the effect of poorly soluble particulate materials (PMs) on lung injury has been widely noted, although crystalline silica particulates are well known to induce tumors in the lung. Many PMs were thought to have low acute toxicity and no genotoxicity. However, inflammation, fibrosis, and metaplasia are induced in rat exposed to chronic inhalation of PMs (Nikula et al., 1997). Nikula (2000) reviewed the list of PMs that increased the incidence of hyperplasia and adenocarcinoma. It is therefore important to decrease PMs in the atmosphere.

The aim of the present study, therefore, is to determine the origin of PMs by measurement of lead isotopes, and to search how to decrease not only PMs but also lead concentrations in the atmosphere.

2 Materials and Methods

2.1 Sample collection:

PMs (PM-1: >10 μm, PM-2: 10 - 2.5μm, PM-3: <2.5μm) were collected with high-volume air samplers (Personal Cascade Impactor Sampler, Tokyo Dylec Co., Tokyo, Japan) on a quartz fiber filter (Pallflex high-purity quartz fiber filter, Pall Co., N.Y., U.S.A.) with a flow rate of 20 l/min, respectively. The sampling site was on the roof of an office building of Kinki University (25 m in height), in Osaka, Japan and the sampling period was one week a month for each sample from May 2003 to January 2004.

2.2 Lead isotope ratio analysis:

The filter was put on a Teflon beaker and 10 ml of conc. nitric acid was added. After heating at 160 °C for 2 hours, 1 ml of perchloric acid was added and the beaker was heated at 160 °C for 1 hour. The same procedure of the addition of nitric acid and perchloric acid was repeated again and the filter was removed. The solution was concentrated to 1 ml by heating, and then, adjusted to 20 ml by the addition of pure water. An inductively coupled plasma mass spectrometer (ICPM-8500, Shimadzu Co., Kyoto, Japan), equipped with a miniaturized torch, was utilized. The operating conditions are listed in Table 1. Lead isotope levels were standardized using NIST Reference Material 981 (National Institute of Standards & Technology, MD, U.S.A.).

Table 1. ICP-MS operating condition

RE power	1.2	kW
Ar plasma gas	7	L/min
Ar auxiliary gas	1.5	L/min
Ar carrier gas	0.62	L/min
Sample depth	5	mm
Measured mass number	Pb	206, 207, 208
Internal standard	Pt	50 ppb

3 Results and Discussion

The increase of anthropogenic activity increases the consumption of heavy metals including lead, and these metals are gradually accumulated in the surface environment. Recently, fine particles like coal dust, diesel exhaust and nickel oxide are reported to have lung cytotoxicity under chronic inhalation, although those particulates were once thought to have low toxicity (Nikula, 2000).

Table 2 shows the average lead concentration of PMs collected for one week a month over nine

months. The average lead content in PM-1, PM-2, and PM-3 did not differ from each other, although the content in PM-2 varied widely. Zheng et al. (2004) showed the concentration of lead in PM10 fractions in Shanghai from 2001 to 2002, and the value was 3948 μg/g. Lead concentrations in the present study was a little lower but not significantly, when lead contents from PM-1 to PM-3 for each month were added. Therefore, there may not be much difference in lead concentration in airborne particulate between Osaka in Japan and Shanghai in China.

Table 2. Lead concentrations in PMs

PMs in atmosphere were collected for one week a month and lead concentrations in PMs were measured in each month. Mean ± S.D.

	Lead concentration (mg/g dry weight)		
PM-1	0.758	±	0.287
PM-2	1.460	±	0.757
PM-3	0.996	±	0.155

The lead isotope ratio is useful to determine the source of lead. In the geological field, older lead ores have lower $^{206/204}$ Pb, $^{206/207}$ Pb, and $^{206/208}$ Pb ratios than recently formed lead ores. Gulson et al. (1995) observed the human health risks of lead exposure in Australians using $^{206/204}$ Pb ratios, as the ratio in both environmental lead sources and blood in mainland Australians is less than 17.0, and the ratios in the blood samples collected from people immigrating from Eastern Europe and the former Soviet Union is greater than 17.5. In addition, Precambrian $^{206/207}$ Pb in Australia is less than 1.04 and is exported all over the advanced nations. Therefore, the $^{206/207}$ Pb ratio in lead imported countries shows lower than their native level (Bindler et al., 2004).

Table 3 shows the average ratios of lead isotopes over nine months in an eastern part of Osaka. In the 1980s to 1990s, there were several reports measuring lead isotopes in aerosols in Japan, shown in Table 4. The ratios of lead isotopes in the present study are different from the previous data. However, Zheng et al. (2004) recently reported that the ratio of $^{207/206}$Pb in airborne particles in Shanghai, China, from 2002 to 2003 was 0.8608 ± 0.0018 and $^{208/206}$Pb was 2.105 ± 0.005. And the ratios of vehicle exhaust particles collected in 1999 were 0.8854 ± 0.0074 in $^{207/206}$Pb and 2.145 ± 0.006 in $^{208/206}$Pb, similar to our present data. Furthermore, the data of $^{207/206}$Pb and $^{208/206}$Pb in the present study is very similar to the data in Dalian and Changchun in China measured by Mukai et al. (2001) from 1996 to 1997. There are several Pb ore with a $^{207/206}$Pb ratio higher than our data as referred for Wong and Li (2004); 0.940 at British Columbia in Canada, 0.951 at Idaho in U.S.A., 0.964 at Broken Hill in Australia, 1.087 at Ontario in Canada. Lead ore in northern China also shows high ratios of $^{207/206}$ Pb and $^{208/206}$ Pb, at 0.93 and 2.22, respectively (Mukai et al., 1993). In addition, Korean lead ore showing relatively higher values of lead isotopes is suggested to contribute to airborne lead in Seoul through industrial activities (Mukai et al., 1993). Therefore, these ratios in PMs increase when those ores are used in Japan.

Table 3. Ratios of lead isotopes in total PMs in each month

$^{207/206}$ Pb	0.880	±	0.011
$^{208/206}$ Pb	2.137	±	0.033
$^{207/208}$ Pb	0.413	±	0.007

mean ± S.D.

Next, we observed the change of lead isotope ratio in each PM depending on the month (Fig. 1). In PM-1 and PM-2, both ratios of $^{207/206}$ Pb and $^{208/206}$ Pb changed similarly from May 2003 to January 2004. In contrast, both ratios in PM-3 dramatically rose and fell over the nine months. As many researchers suggested, multiple lead sources comprise the lead in atmospheric environments. Mukai et al. (1993) observed that lead isotope ratios in the Japanese atmosphere were close to those of fly ash from refuse incinerators, but they also suggested that lead isotopes in the atmosphere consist of mixes of various lead sources. Nevertheless, from the result that both ratios of lead isotopes in PM-3 change every month, the sources of lead isotopes in PM-3 may differ from those of PM-1 and PM-2. Gwiazda & Smith (2000) suggested that the co-linearity of $^{208/206}$ Pb versus $^{207/206}$ Pb reflected major ores as the ultimate source in the early 20 C, but recently, the increased use of recycled lead has blurred the isotopic differences of lead. And there was a significant correlation between $^{208/206}$ Pb and $^{207/206}$ Pb in PM-1 ($r=0.7071$, $p<0.05$). On the contrary, there were no relationship between $^{208/206}$ Pb and $^{207/206}$ Pb in PM-2 and PM-3 in the present study (r=0.5355 in PM-2; r=0.4120 in PM-3, respectively). Therefore, it is strongly suggested that the lead isotopes in PM-3 consist of various sources of lead like recycled lead, coal, and refuse incinerator ash.

It is of interest that aerosols in the cities of eastern China and Korea showed relatively high values of lead isotope ratios (Mukai et al., 1993), and these values are similar to the present data. Further studies of lead isotopes needs to analyze atmospheric pollution across East Asia including Japan.

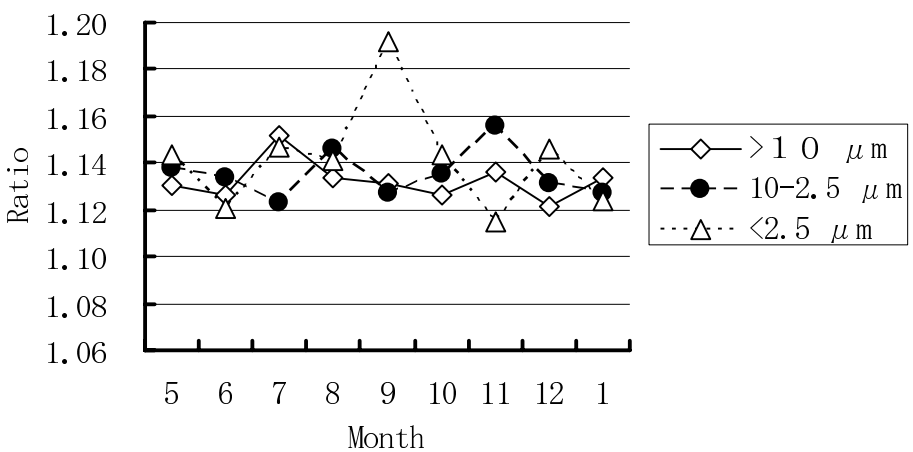
In conclusion, the analysis of lead isotope ratios in atmospheric particulates is useful to know the status of environmental pollution, although the identification of lead origins is difficult. A continuous and global study in East Asia area is needed.

Table 4. Data of lead isotope ratio in aerosols in Japan published previously

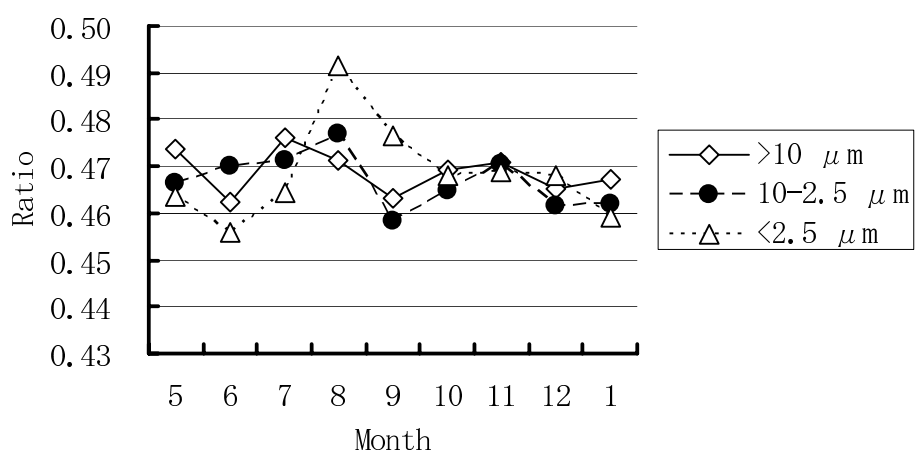
	$^{207/206}$Pb	$^{208/206}$Pb
8 cities in Hokkaido [a]		
1981	0.8611 ± 0.0050	2.088 ± 0.020
Western part of Tokyo [b]		
Oct. 1979 - Feb. 1981	0.8630 ± 0.0002	2.1049 ± 0.0004
Feb. 1981 - May 1982	0.8538 ± 0.0002	2.0877 ± 0.0005
May 1982 - Jan. 1983	0.8646 ± 0.0002	2.1055 ± 0.0004
7 cities in Japan [c]		
1988 - 1989	0.8630 ± 0.0039	2.0993 ± 0.0137
Tsukuba [d]		
summer 1997	0.863 ± 0.000	2.107 ± 0.004

[a] Murozumi et al., 1982; [b] Hirao et al., 1986; [c] Mukai et al., 1993; [d] Mukai et al., 2001.

(a) Pb 206/207



(b) Pb 206/208



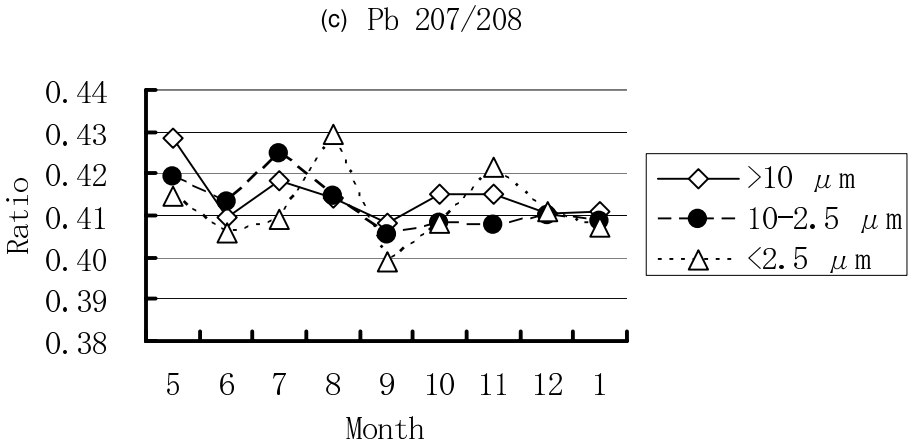


Fig. 1 Change of ratios of lead isotopes in PMs from May, 2003, to January, 2004.
PMs were divided into three groups depending on their particle sizes, PM-1 ($> 10\mu\mathrm{m}$), PM-2 (10-2.5$\mu\mathrm{m}$), and PM-3 ($< 2.5\mu\mathrm{m}$).

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