

Estimation of lead sources in a Japanese cedar ecosystem using stable isotope analysis

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Abstract

Anthropogenic Pb affects the environment worldwide. To understand its effect on forest ecosystem, Pb isotope ratios were determined in precipitation, various components of vegetation, the forest floor, soil and parent material in a Japanese cedar (*Cryptomeria japonica* D. Don) forest stand. The average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in bulk precipitation was 1.14 ± 0.01 (mean \pm SD), whereas that in the subsoil (20–130 cm) was 1.18 ± 0.01 . Intermediate ratios ranging from 1.15 to 1.16 were observed in the vegetation, the forest floor, and the surface soil (0–10 cm). Using the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, the contribution of anthropogenic sources to Pb accumulated in the forest were estimated by the simple binary mixing model. Sixty-two percent of the Pb in the forest floor, 71% in the vegetation, and 55% in the surface soil (0–10 cm) originated from anthropogenic sources, but only 16% in the sub-surface soil (10–20 cm) was anthropogenic. These results suggest that internal Pb cycling occurs mainly between surface soil and vegetation in a Japanese cedar ecosystem, and that anthropogenic Pb strongly influences Pb cycling. Although the Japanese cedar ecosystem has a shallow forest floor, very little atmospherically derived Pb migrated downward over 10 cm in depth.

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1. Introduction

Lead consumption has increased dramatically in the last 50 a owing to its use as a gasoline additive (Adriano, 2001). Despite its declining use in many countries, including Japan, Pb is still released to the atmosphere from mining, smelting, fossil fuel combustion, various industrial processes, waste incineration, and automobiles (Nriagu, 1990;

Adriano, 2001). In continental Asia, emissions have been increasing and are now the highest in the world (Pacyna and Pacyna, 2001).

Atmospheric deposition is the major pathway of Pb input into forest ecosystems, and most of the deposits are derived from anthropogenic emission sources (Nriagu, 1989; Shirahata et al., 1980). However, the Pb output from forest ecosystems is considerably lower than the input, which occurs through stream discharge (Heinrichs and Mayer, 1980; Turner et al., 1985). Consequently, most atmospheric-derived Pb is retained within vegetation, the forest floor, and the soil (Heinrichs and Mayer, 1980; Smith and Siccama, 1981; Friedland

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and Johnson, 1985; Miller and Friedland, 1994). Among these components, significant accumulation of Pb is often observed in the surface soil layer and the forest floor. This is because Pb has a strong affinity for organic matter (Adriano, 2001), which results in a long residence time. For example, in North America and Europe, the residence times in the forest floor have been estimated as 17–500 a (Miller and Friedland, 1994; Bindler et al., 1999; Kaste et al., 2003).

In nature, Pb has four stable isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb . Since the Pb isotopic compositions are distinct between anthropogenic Pb in airborne particulate matter and geogenic Pb in deep soil profiles (Hansmann and Köppel, 2000), several studies have used these differences to determine the origins of Pb accumulated in forest soils and peat bogs (Bindler et al., 1999; Nowack et al., 2001; Hernandez et al., 2003; Haack et al., 2003; DesJardins et al., 2004). The isotope method has confirmed that large quantities of Pb in the surface soil layers and forest floor originated in airborne particles. Watmough and Hutchinson (2004) reported that approximately 60% of Pb in the surface soil, 75% in the forest floor, and 65–100% in vegetation was derived from anthropogenic sources, in a rural woodland in Ontario, Canada. This means that the Pb accumulated in the surface soil had different sources, not only airborne particles but also geogenic origins, which suggests that biogeochemical cycling is important for understanding Pb dynamics in forest ecosystems. Thus, different ecosystems would have different characteristics of Pb cycling owing to predominant vegetation, soil type and geology. For example, in North American and European forests, where several studies have been conducted, a thick forest floor functions as a reservoir of Pb in the ecosystem (Heinrichs and Mayer, 1980; Friedland and Johnson, 1985; Turner et al., 1985; Miller and Friedland, 1994). In temperate Japanese forests, however, the thinner forest floor limits Pb accumulation (Itoh et al., 2005). Thus, the behavior of atmospheric-derived Pb in Japanese forest ecosystems might be distinct from that in North America and Europe.

The objective of this study was to estimate the sources of Pb accumulated in a Japanese cedar forest ecosystem using Pb isotope analysis. To determine the contribution of anthropogenic Pb in the forest ecosystem which will allow assessment of anthropogenic impacts on the environment.

2. Materials and methods

2.1. Site descriptions

The study was conducted at the Katsura Experimental Field ($36^{\circ}32'N$, $140^{\circ}18'E$), located in a hilly area about 120 km NE from the center of Tokyo, at about 250 m a.s.l. The mean annual temperature is 13.0°C and the mean annual precipitation is 1500 mm. A 38-year-old stand of Japanese cedar (*Cryptomeria japonica* D. Don) planted on the middle and lower slopes was studied. Japanese cedar is a popular tree for plantation, occupying about a quarter of forests in Japan. The soil at the site is mainly derived from thick volcanic ashes deposited approximately 32 ka ago, and is classified as Brown Forest Soil according to the Classification of Forest Soil in Japan (Forest Soil Division, 1976) and as a Cambisol according to the FAO/Unesco soil classification system (FAO/Unesco, 1990). The bedrock of this area is sedimentary rock from the Mesozoic and Paleozoic eras.

2.2. Sampling

Bulk precipitation was collected monthly in an open area adjacent to the study site for a year (April 2002–April 2003); a total of 12 samples were analyzed. Five Japanese cedar trees at the site were cut down to collect samples of stem wood, bark, branches, and needles. Forest floor, composed of loosely accumulated L and F layers approximately 4 cm in thickness, was collected by using a frame (50×50 cm) at three positions. Bulk soil samples were taken from each horizon of one soil profile excavated to 130 cm in the stand. Bedrock samples were collected at outcrops along a stream near the site. To minimize contamination and alteration by runoff water and air, fresh rock samples were taken after excavating about 20 cm from the surface of the outcrops.

2.3. Sample treatment

The bulk precipitation samples were passed through a $0.45\text{-}\mu\text{m}$ membrane filter and acidified with HNO_3 (1:100 v/v). The vegetation and forest floor samples were oven-dried to constant weight at 70°C . The soil samples were dried at room temperature and sieved through a 2-mm sieve. All samples were ground in an agate mortar.

2.4. Digestion procedure and chemical analysis

Ground samples of the vegetation and forest floor (0.4 g) and 0.5 g of soil samples were digested with purified 68%-HNO₃ (5 mL) and 36%-HCl (1 mL) in a microwave oven (Multiwave 3000, Anton-paar, Austria) for trace metal analysis. After digestion, the sample was transferred to a polyethylene volumetric flask (50 mL) and made up to the mark with Milli-Q water. Before analysis, the samples were diluted (1:10 v/v) in 5% HNO₃.

Lead isotopes (²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb) were measured by inductively coupled plasma mass spectrometry (ICP-MS; Platform-ICP, Micromass, UK). NIST 981 (common lead isotopic standard) was used to check the accuracy of the measurements. The average ²⁰⁶Pb/²⁰⁷Pb ratio measured was 1.093 ± 0.004 (n = 6), with a relative standard deviation (RSD) of 0.4% (certified ²⁰⁶Pb/²⁰⁷Pb ratio is 1.093 ± 0.001).

2.5. Estimation of anthropogenic lead contribution

The relative proportions of atmospherically and geologically derived Pb in the components of the forest ecosystem were calculated using the end member method (Shotyk et al., 1997; Bindler et al., 1999). A simple binary mixing model was used:

Atmospherically-derived Pb(%)

$$= \frac{{}^{206}\text{Pb}/{}^{207}\text{Pb sample} - {}^{206}\text{Pb}/{}^{207}\text{Pb geogenic}}{{}^{206}\text{Pb}/{}^{207}\text{Pb atmospheric} - {}^{206}\text{Pb}/{}^{207}\text{Pb geogenic}} \times 100 \tag{1}$$

where ²⁰⁶Pb/²⁰⁷Pb sample is the ²⁰⁶Pb/²⁰⁷Pb ratio of the sample in the forest ecosystem, ²⁰⁶Pb/²⁰⁷Pb geogenic is the ²⁰⁶Pb/²⁰⁷Pb ratio of the geogenic Pb, and ²⁰⁶Pb/²⁰⁷Pb atmospheric is the ²⁰⁶Pb/²⁰⁷Pb ratio of the atmospheric Pb.

For geogenic Pb, the mean ²⁰⁶Pb/²⁰⁷Pb ratios of subsoil (20–130 cm) were used, because volcanic deposits on the bedrock constitute the predominant parent material of the soil in the stand. For atmospheric Pb, the mean ²⁰⁶Pb/²⁰⁷Pb ratios of bulk precipitation were used. From 96% to 99% of total Pb in bulk precipitation is derived from anthropogenic origins (Shirahata et al., 1980; Nriagu, 1989).

3. Results

3.1. Lead isotope ratios in a Japanese cedar ecosystem

The ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios of needles, bark, stem wood, branches, cones, forest floor, soil, bedrock, and bulk precipitation in the Japanese cedar ecosystem are shown in Fig. 1. The

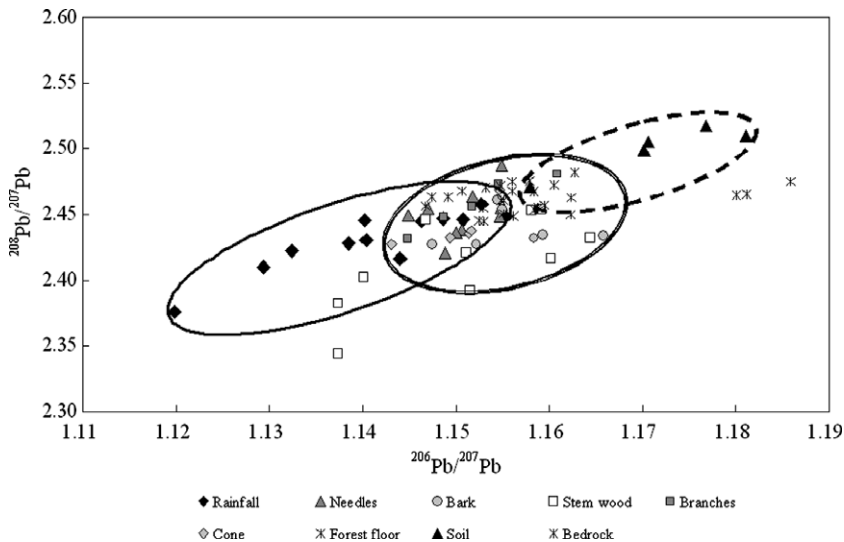


Fig. 1. Lead isotope ratios (²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb) in the Japanese cedar ecosystem. A single-line circle shows the range of the Pb isotope ratios in bulk precipitation samples, a double-line circle shows the range in vegetation and forest floor samples, and a broken-line circle shows the range in forest soil samples. Some of the stem wood and bedrock samples lie out of the ranges above.

$^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios of the rainfall samples were low, ranging from 1.12 to 1.16 and from 2.38 to 2.46, respectively. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the rainfall samples, reflecting those of the airborne particles, were consistent with the previously reported ranges of the isotope ratios of airborne particles in Japan (Mukai et al., 1993). In contrast, the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios of the forest soil samples were high, ranging from 1.16 to 1.18 and from 2.45 to 2.52, respectively. The highest $^{206}\text{Pb}/^{207}\text{Pb}$ ratio occurred in the bedrock, which suggests that the subsoil is composed of a mixture of weathered materials from the volcanic deposits and the bedrock. The ratios of forest floor and vegetation samples were mostly intermediate between those of rainfall and forest soil. Hence, using the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, the components in the forest ecosystem could be divided into three groups: rainfall, forest soil and bedrock, and vegetation and forest floor (Fig. 1).

The vertical distribution of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the Japanese cedar stand is shown in Fig. 2. The average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the bulk precipitation was 1.14 ± 0.01 (mean \pm SD). Although the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the components varied among the vegetation, no significant differences were found; the averages ranged from 1.15 to 1.16. The average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the surface soil (0–10 cm) was lower than that of the sub-surface soil (10–20 cm)

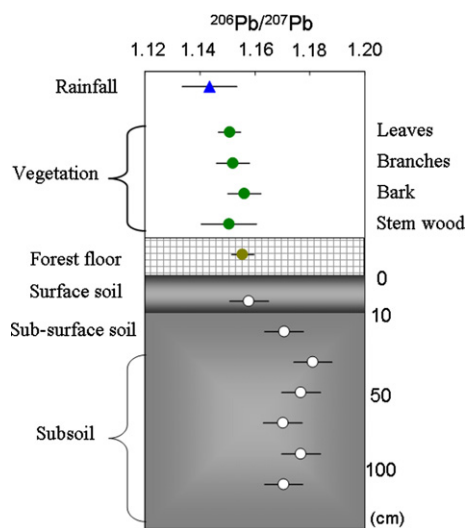


Fig. 2. Vertical distribution of the Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$) in the Japanese cedar ecosystem. Triangle and circles show the mean of Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$). Lateral bars show the standard deviation of Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$) in each component.

and subsoil (20–130 cm). The forest floor had almost the same $^{206}\text{Pb}/^{207}\text{Pb}$ ratio as the surface soil. There was a significant difference ($P < 0.05$, Turkey–Kramer test) in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between bulk precipitation and subsoil.

3.2. Estimation of the contribution of anthropogenic lead to a Japanese cedar ecosystem

According to the simple binary mixing model (Eq. (1)), 55% of Pb in the surface soil (0–10 cm) was derived from the atmosphere, on average. In the sub-surface soil layer (10–20 cm), the contribution of the atmospheric decreased rapidly to 16%. Sixty-two percent of Pb in the forest floor originated from anthropogenic sources. In the vegetation, atmospheric origin was 71% on average, although there were slight differences in the percentages among plant components.

4. Discussion

The $^{206}\text{Pb}/^{207}\text{Pb}$ Pb isotope ratios in the vegetation, forest floor, and surface soil showed intermediate values between those of anthropogenic and geogenic Pb through mixing of these sources by biogeochemical cycling in the ecosystem (Fig. 2). Incorporation of atmospherically derived Pb into vegetation has two possible pathways: direct incorporation in the leaves and bark, and uptake from roots. As Watmough and Hutchinson (2003) reported that Pb incorporation from bark is not likely to be a major pathway to wood, the authors consider that direct incorporation of Pb from bark and needles does not contribute extensively to Pb cycling, because $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in bulk precipitation were significantly lower than those of bark and needles. Lead would be absorbed by roots mostly from the mineral soil, because the forest floor is thin and no fine roots exist in the forest floor. Some Pb in vegetation is returned to the surface soil by litterfall, which establishes the biological cycling of Pb in the forest ecosystem. Thus, vegetational factors such as composition of vegetation, acquisition of Pb, root distribution, and litter production are important for determining Pb cycling in forest ecosystems.

In the forest floor, 55% of Pb was estimated to be of anthropogenic origin at the study site. This is comparable to the result reported by Watmough and Hutchinson (2004), who studied a woodland site with a shallow forest floor. The present study site also has a thin forest floor. In cool-climate

areas, a thick forest floor provides a large Pb pool (Heinrichs and Mayer, 1980; Smith and Siccama, 1981; Friedland and Johnson, 1985; Miller and Friedland, 1994), and the Pb residence time in the forest floor is long, from 17 to 500 a (Miller and Friedland, 1994; Bindler et al., 1999; Kaste et al., 2003). In contrast, at mesic sites planted with Japanese cedar, Pb has a short residence time in the forest floor. According to Itoh et al. (2005), the residence time of Pb in the forest floor is 2.5 a. If the site has a thick forest floor of the mor or moder type, atmospherically derived Pb may contribute significantly, because Pb has a long residence time in such a forest floor.

The Pb in the forest floor is likely to migrate rapidly to the surface soil layer because of quick litter decomposition. The Pb isotope ratios in the mineral soils suggest that Pb from the decomposing forest floor permeates only into the surface soil (0–10 cm) (Fig. 2), probably because of the high affinity of Pb for soil organic matter. A high C content (120.7 mg g⁻¹, S. Aizawa, personal communication) in the surface soil, which seems to be influenced by volcanic ash, may prevent Pb from migrating downward a long distance. Organic matter and mineralogical characteristics in the soil would influence the Pb dynamics of the ecosystem.

5. Conclusion

Stable isotope analysis revealed biogeochemical cycling of Pb in a Japanese cedar forest ecosystem in central Japan. On average, 71% of Pb in the vegetation originates from the atmosphere. In the forest floor, atmospherically derived Pb contributes 62% of total Pb. Lead has a short residence time of 2.5 a in this forest floor, and decomposing forest floor migrates to the surface soil, where most of the atmospherically derived Pb is retained. In the sub-surface soil (10–20 cm deep), only 16% of Pb originated in the atmosphere. These results indicate that internal cycling occurs between surface soil and vegetation, but that external input of atmospherically derived Pb of anthropogenic origin strongly influences the internal Pb cycling in the forest ecosystem.

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