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Lead Isotope Systematics in Polytrichum formosum: An Example from a Biomonitoring Field Study with Mosses

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With the aid of inductively coupled plasma mass spectrometry (ICP-MS), $^{206/207}$Pb isotope ratios were determined in 34 moss samples (*Polytrichum formosum*) taken from the Hoerner Bruch area near Osnabrück (FRG) in the years 1987−1996. The goal was to distinguish different sources of atmospheric lead pollution by the investigation of lead isotope ratios. Reproducibility tests were carried out to ensure the reliability of analyzing Pb isotope ratios in moss samples by means of quadrupole ICP-MS. The reproducibility of the isotope ratios for one digested sample and the day-to-day reproducibility were determined. In all the moss samples analyzed, relative standard deviations of <0.26% for five replicate measurements of one digested sample were achieved for the $^{206/207}$Pb isotope ratios. On the basis of the $^{206/207}$Pb isotope ratio, it was possible to establish that the sources of man-made atmospheric inputs of lead have changed over the 10-year period investigated. In the moss samples analyzed, the $^{206/207}$Pb isotope ratio was found to have risen significantly from 1.131 in 1987 to 1.154 in 1996. This increase in the $^{206/207}$Pb isotope ratio can be attributed to a reduction of atmospheric inputs of lead from petrol.

Introduction

One of the most widespread contaminants in our environment is the element lead. Besides metallurgy (metal refining) and the burning of refuse and coal, the worldwide distribution of lead is the result of its use as a fuel additive and the consequent emissions from traffic (combustion of alkyl-leaded petrol). This means that atmospheric lead deposition has a complex mixture of sources varying in time and space. Lead has four stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. The isotope ^{204}Pb is not of radiogenic origin. The isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb are end products of the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th with a half-life of 4.5, 0.7, and 14 billion years, respectively. Additionally, lead of primordial isotopic composition (*1*) was incorporated into the geosphere during the formation of the earth about 4.5 billion years ago. Lead ores used for human activities, especially in gasoline additive production, in Europe is mostly imported from

Australian and Canadian Precambrian ores with $^{206/207}$Pb ratios between 1.04 and 1.10 (*2*). Lead naturally derived from local rocks and soils in Germany is characterized by $^{206/207}$Pb isotope ratios of 1.18−1.22 (*3*). This means that analyses of isotope ratios can be used to differentiate between geogenic and anthropogenic inputs of the element lead into the environment if both components were not mixed and homogenized before.

Since the development of high-resolution thermal ionization mass spectrometers (TIMS) by Nier in the late 1930s (*4*), studies of lead isotopes have been common in many fields of geology (crust-mantle processes, geochronology, geochemistry, ore prospection and mining, and many others); for reviews, see Doe (*5*) and Faure (*6*). The introduction of inductively coupled plasma mass spectrometry (ICP-MS) in 1983 (*7*) opened up comparatively easy (quick) access to the measurement of isotope ratios, but ICP-MS does not equal TIMS in respect of precision.

The usefulness of isotope ratio measurement for tracing environmental pollution (performed either by conventional TIMS or by ICP-MS) has been demonstrated in several publications in the last 10 years, and special attention is devoted to the element lead. Lead isotope studies have been put to several applications in environmental research. Examples are traffic fuel emissions (*8*), U.S. gasoline and aerosols (*9*), air aerosols (*3, 10−12*), lake water (*13*), lake sediments (*2, 14*), soil (*15*), peat bogs (*16−18*), and Greenland Ice (*19*). Carignan and Gariépy (*20*) reported on the use of the isotope composition of atmospheric lead in epiphytic lichens as a tracer of pollution source. One recently published work reports on the isotopic character of lead deposited from the atmosphere at a grassland site since 1860 (*21*).

The last 20 years have seen widespread use of mosses in biomonitoring to record air pollution with heavy metals or acid rain components (*22−26*). Recent publications (*27−29*) show the effectiveness of mosses for large-scale monitoring. For lead, the capacity of moss tissues to sorb traces of this metal was found to be very high (*30*). The global distribution of mosses in suitable amounts and their easy identification in the field enables them to be used as a standardized method in air quality monitoring programs. Especially for lead, a significant correlation was found between the element content in moss species and precipitation data (*31*).

This paper investigates whether it is possible to differentiate between various sources of atmospheric lead inputs over a period of 10 years by measuring lead isotope ratios ($^{206/207}$Pb) in the biomonitor *Polytrichum formosum* (an endohydric moss).

Materials and Methods

Sampling. The moss samples were taken from a 30−40-year-old spruce forest (Hoerner Bruch) southeast of Osnabrück (F.R.G.). Starting in September 1985, samples were taken regularly (usually at weekly intervals) from 50 to 100 individual plants of *P. formosum* on an area of approximately 1 m² and made up into a mixed sample. The individual samples were picked about 1 cm above the soil. These samples represent a period of time of 2−3 years, and the content of metals reflected a measure of the atmosphere deposition during that period (*32*). Gloves were worn during sampling, and only synthetic materials were used. Attention was given to pick the moss samples without soil contamination. Markert and Weckert (*33−35*) have given detailed descriptions of the moss *P. formosum* in this area, which means that a large amount of background information was available. These investigations showed that it was sufficient to measure lead

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TABLE 1. Operating Parameters of the Elan 5000 ICP-MS for Measuring the $^{206/207}$Pb Isotope Ratio

ICP parameters		MS parameters	
coolant gas flow	15 L/min	dwell time	20 ms
auxiliary gas flow	0.8 L/min	sweeps/replicate	1000
carrier gas flow	0.95 L/min	replicate time	20 000 ms
		points/peak	1
forward power	1100 W	replicates	5
nebulizer type	cross-flow	sampler	platinum
pump rate	1.0 mL/min	skimmer	platinum

isotope ratios in four regularly selected samples per year (spring, summer, autumn, and winter).

Preparation of the Samples. After the samples (total weights 1–2 g) had been gathered, they were frozen at −20 °C to await further processing. In accordance with an international agreement, the samples were not cleaned by washing (36). Before digestion, they were dried at 40 °C to constant weight. For storage, the samples were welded into cleaned polyethylene bags. From the dried samples, an aliquot (150–200 mg) was mixed with 4 mL of 65% HNO$_3$ suprapur (Merck) and 1 mL of 30% H$_2$O$_2$ suprapur (Merck). Digestion was carried out in PFA vessels in a CEM MDS-2000 microwave oven (40 psi/1 min; 80 psi/1 min; 150 psi/10 min). After digestion, the solution was made up to 20 mL with deionized H$_2$O.

Because of the small natural differences in the Pb isotope ratios, it is essential to avoid contamination at all stages of sampling, of sample preparation, and during the analytical process. To ensure that the samples were not contaminated with lead, blank readings were taken following the same procedure as the one used for unknown samples and were found to be below the detection limit of 0.3 ng/mL Pb.

Sample Measurements. In this study, the $^{206/207}$Pb isotope ratio was measured by inductively coupled plasma quadrupole mass spectrometry (Elan 5000 ICP-MS from Perkin-Elmer/Sciex). The analytical parameters—dwell time, sweeps/replicates, and replicates—had to be optimized. The values to be obtained were the relative standard deviation and the total measuring time. The operating parameters of the Elan 5000 ICP-MS are shown in Table 1.

Reproducibility was determined with the aid of the standard reference material SRM 981—Common Lead Isotopic Standard—from the National Institute of Standards and Technology (NIST). The mass bias of the sequentially measuring ICP-MS was also corrected with SRM 981 as recommended by Russ and Bazan (37) and Krause et al. (3). It was done by analyzing SRM 981 (100 ng/mL Pb in the same acid matrix as the one used for the digested and diluted moss samples) after every second moss sample. A concentration of ca. 100 ng/mL was adjusted in the final solution of the digested moss samples also. The frequent measurement of SRM 981 was a good means of ascertaining drift effects. A comparison of the $^{206/207}$Pb isotope ratios determined with the ICP-MS with the certificate of SRM 981 (1.0933) (38) showed that factors of 1.0056–1.0070 (which means that values ranged from 1.0857 to 1.0872 for the ^{206}Pb/^{207}Pb ratio) had to be used to correct the mass bias. The achieved relative standard deviation of all analyzed SRM 981 solutions (five replicate measurements) was ≤0.2%.

The lead content of the dried and digested samples was determined by an atomic emission spectrometer with an inductively coupled plasma. A detailed description of the analytical conditions is given by Markert and Weckert (34).

Accuracy of the Lead Measurement. Standard reference materials (GBW 8501 [peach leaves] and BCR 414 [trace elements in plankton], Promochem Ltd., Germany) were used to check whether the chosen digestion method was suitable

TABLE 2. Measurement of Pb in the SRMs GBW 8501 and CRM 414

SRM	certificate (μg/g)	first result with ICP-MS (μg/g)	second result with ICP-MS (μg/g)
GBW 8501, peach leaves	0.99 ± 0.08	0.99 ± 0.15	0.98 ± 0.01
CRM 414, plankton	3.97 ± 0.19	3.75 ± 0.06	3.97 ± 0.03
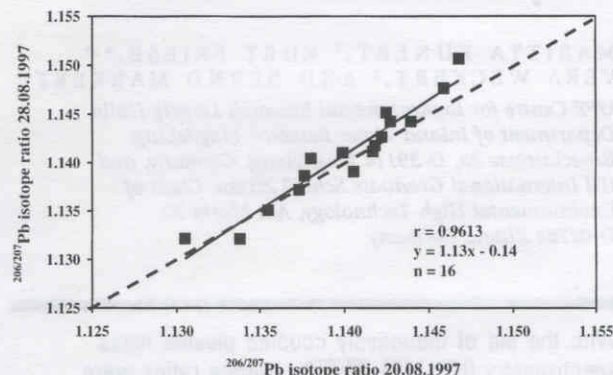
FIGURE 1. Day-to-day reproducibility of ^{206}Pb/^{207}Pb isotope ratio measurements in moss samples on August 20 and 28, 1997.

for measuring lead in plant samples and whether it was possible to achieve accurate and reproducible analytical values in the mosses with ICP-MS. The results in Table 2 show that it was indeed possible to achieve reproducible and accurate results with the chosen analytical method (digestion in a microwave field and analysis by ICP-MS).

Test for Reproducibility. To check the reproducibility of the $^{206/207}$Pb isotope ratios obtained by ICP-MS, the isotope ratio of a selection of 16 samples was determined on different days (August 20 and 28, 1997). To exclude drift effects, the sequence of the samples to be analyzed was determined on a random basis for the second series of measurements on August 28. The results in Figure 1 show a good agreement between the two series. The coefficient of correlation value obtained was 0.9613. The F- and t-tests ($P = 0.99$) revealed that no significant difference was detectable between 15 of the 16 analyzed samples.

Figure 2 shows the reproducibility of different digestions of one moss sample. Markert and Weckert (33) established that the heavy metal content of 50–100 moss samples of one sampling site showed no significant difference without additional homogenization. These investigations (Figure 2) confirm the homogeneity of the sampling material (150–200 mg) and the reproducibility of the correction of mass bias with SRM 981.

Results and Discussion

$^{206/207}$Pb Isotope Ratios in the Moss Samples Collected from 1987 to 1996. Table 3 show the development of the $^{206/207}$Pb isotope ratios in the moss samples from the Hoerner Bruch site near Osnabrück over the years 1987–1996. The lead concentrations in these samples are shown in Figure 3. The $^{206/207}$Pb isotope ratio in the samples of *P. formosum* increases from 1.131 in October 1987 to 1.154 in July 1996 (Table 3). The F- and t-tests ($P = 0.99$) revealed a significant difference between the isotope ratios of the years 1987 and 1996. The isotope ratio in the samples was found to have increased almost continuously from 1987 to 1990 (from 1.131 to 1.144). Between 1991 and 1994, the isotope ratios change only slightly. The values measured were between 1.142 and 1.148. The isotope ratio was then found to have increased again, from 1.148 to 1.154, in the years 1995–1996.
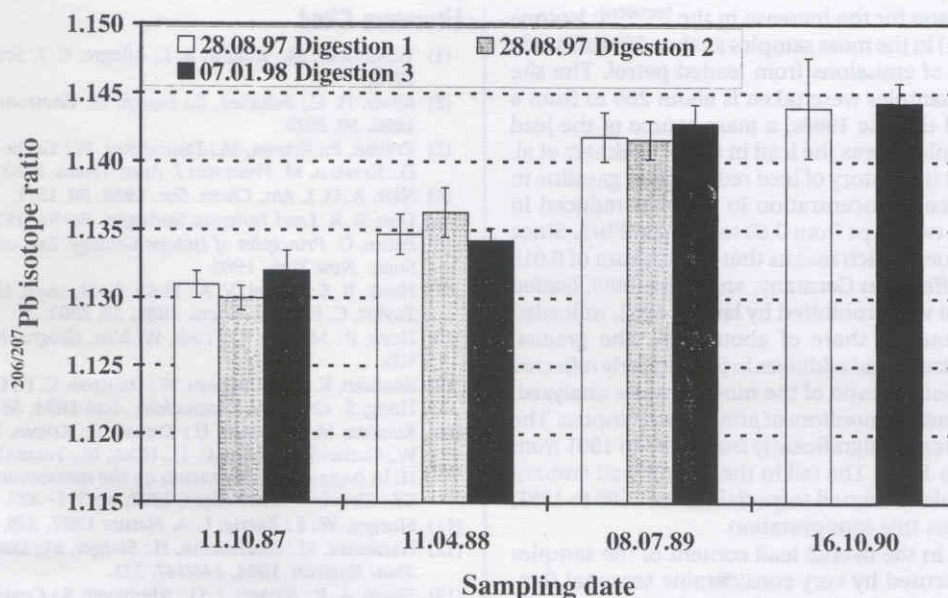
FIGURE 2. Reproducibility of $^{206/207}$Pb isotope ratio measurements in mosses in three different solutions. The date of the analysis is shown in the key. The error bar is the standard deviation of the five replicates. Only two digestions were analyzed from the sample of October 16, 1990.

TABLE 3. $^{206/207}$Pb Isotope Ratios in the Moss Samples from the Hoerner Bruch Site near Osnabrück from 1987 to 1996[a]

sampling date	$^{206/207}$Pb isotope ratios	standard deviation
11.10.1987	1.131	0.0009
02.01.1988	1.134	0.0018
11.04.1988	1.136	0.0015
10.07.1988	1.137	0.0013
09.10.1988	1.138	0.0015
07.01.1989	1.138	0.0008
01.04.1989	1.141	0.0014
08.07.1989	1.142	0.0018
01.10.1989	1.140	0.0014
06.01.1990	1.142	0.0003
01.04.1990	1.142	0.0014
01.07.1990	1.143	0.0017
16.10.1990	1.144	0.0037
05.01.1991	1.142	0.0013
01.04.1991	1.146	0.0023
15.10.1991	1.147	0.0009
05.01.1992	1.146	0.0023
04.04.1992	1.144	0.0016
05.07.1992	1.146	0.0015
10.10.1992	1.147	0.0006
01.04.1993	1.144	0.0016
16.07.1993	1.145	0.0009
17.10.1993	1.146	0.0025
02.01.1994	1.147	0.0013
27.03.1994	1.143	0.0012
08.07.1994	1.146	0.0007
08.10.1994	1.148	0.0014
06.01.1995	1.148	0.0008
24.03.1995	1.148	0.0007
11.07.1995	1.146	0.0006
08.10.1995	1.150	0.0009
14.01.1996	1.153	0.0019
31.03.1996	1.151	0.0016
06.07.1996	1.154	0.0004

[a] The standard deviation resulted of the five replicate measurements of one digested sample. Dates are given as day, month, and year.

Discussion. A number of studies using different kinds of samples have confirmed that manmade pollution sources can be revealed by means of the $^{206/207}$Pb isotope ratio (10, 11, 19–21). Krause et al. (3) discovered that the various oil companies in Germany buy their tetraethyl lead from a
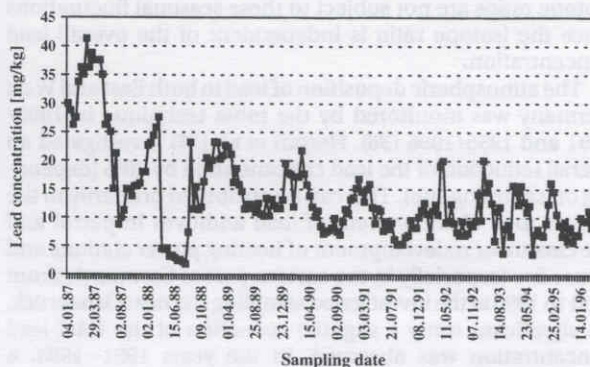

FIGURE 3. Lead concentrations in the moss samples from the Hoerner Bruch site near Osnabrück from 1986 to 1996 (30).

common pool. $^{206/207}$Pb isotope ratios between 1.095 and 1.105 were analyzed in petrol. Kersten et al. (10) demonstrated that the Australian ores used for making tetraethyl lead have a $^{206/207}$Pb isotope ratio of 1.04 and that Canadian ores have isotope ratios of 1.07–1.16. Monna et al. (39) give $^{206/207}$Pb isotope ratios of 1.17–1.20 as background values for pre-industrial sediments in France and the U.K., whereas the lead introduced by industrial processes has an isotope ratio of 1.134–1.155. Hamester et al. (12) could distinguished between two different sources of atmospheric pollution using stable lead isotope measurements. In samples originating from vehicle-generated aerosols (Elbtunnel, Hamburg), the $^{206/207}$Pb isotope ratios ranged from 1.081 to 1.096, and in samples originating from waste incineration plants (Hamburg), a $^{206/207}$Pb isotope ratio of 1.142–1.159 was analyzed. Krause et al. (3) found geogenic background values of 1.18–1.22 in rock samples from Helgoland (Germany, an island in the North Sea). Bacon et al. (21) analyzed samples taken from a grassland site at Rothamsted (U.K.) from 1860 to 1988. Until 1880, a $^{206/207}$Pb isotope ratio of about 1.170 was found. In 1985, the isotope ratio reached a value of 1.098. The reason for the decrease in the isotope ratio between 1880 and 1940 is probably the importation of ore and coal with low isotope ratios, for example, of Australian origin. The constant decrease of the isotope ratio between 1950 and 1985 was traced back to the use of leaded fuel.

The main reason for the increase in the $^{206/207}$Pb isotope ratio (1987–1991) in the moss samples analyzed in this study is the reduction of emissions from leaded petrol. The site from which the samples were taken is about 200 m from a main road. Until the late 1980s, a main source of the lead accumulated by plants was the lead in petrol. Helmers et al. (40) summarized the history of lead reduction in gasoline in Germany: The lead concentration in fuel was reduced in 1972 and 1976 in two steps from 0.63 to 0.25 g of Pb/L. Since 1986, unleaded fuel (which means that a maximum of 0.013 g of Pb/L) was offered in Germany, and since 1988, leaded low octane petrol was prohibited by law. In 1992, unleaded fuel reached a market share of about 84%. The gradual reduction of the use of lead additives in fuel is clearly reflected by the $^{206/207}$Pb isotope ratio of the moss samples analyzed, which are excellent biomonitors of atmospheric inputs. The isotope ratio increased significantly from 1987 to 1991 from values of 1.131 to 1.147. The fall in the overall lead content of the moss samples analyzed (especially from 1986 to 1991; Figure 3) confirms this interpretation.

The decrease in the overall lead content of the samples is somewhat obscured by very considerable seasonal fluctuations, with maximum concentrations in the winter months and minimum concentrations in summer. The latter can be attributed to a dilution effect caused by the increased productivity of *P. formosum* in spring (30). The $^{206/207}$Pb isotope ratios are not subject to these seasonal fluctuations since the isotope ratio is independent of the overall lead concentration.

The atmospheric deposition of lead in both East and West Germany was monitored by the moss technique in 1990/1991 and 1995/1996 (36). Herpin et al. (36) investigated an overall reduction of the lead concentration by 40% (depending on sampling site). This can be attributed primarily to the almost total abandonment of lead additives in petrol and the closure or redevelopment of heating power stations and house fire (especially in the eastern part of Germany). From 1991 to 1996 at the investigated sampling site near Osnabrück, no significant (only a slightly) reduction of the total lead concentration was observed. In the years 1991–1994, a $^{206/207}$Pb isotope ratio of about 1.145 was analyzed. An increasing isotope ratio from 1.148 to 1.154 was measured in the years 1995–1996. Because of the almost total reduction of the emission of leaded gasoline, the main reason for this was thought to be that other sources such as industrial processes became preponderant. The measured isotope ratios in mosses are comparable with the isotope ratios investigated by Hamester et al. (12) in samples originated from waste incineration plants (Hamburg). Monna et al. (39) published similar $^{206/207}$Pb isotope ratios of 1.143–1.155 for inputs of lead from industrial processes in the U.K. and France.

There are no geogenic measurements from soil samples in the area from which the samples were taken. However, various authors state values between 1.17 and 1.22 for recent soils in Germany (3) and France and the U.K. (39), which means that the $^{206/207}$Pb isotope ratios found in the moss samples in 1996 probably indicate an anthropogenic influence through industrial processes. It became clear that a change in the sources of atmospheric inputs (leaded gasoline, industrial lead, and geogenic lead) of lead over a period of 10 years can be demonstrated by measuring lead isotope ratios ($^{206/207}$Pb) in the biomonitor *P. formosum*.

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