

# Pb isotopes as a reliable marker of early mining and smelting in the Northern Harz province (Lower Saxony, Germany)

F. Monna<sup>a,b,c,\*</sup>, K. Hamer<sup>b</sup>, J. Lévêque<sup>c</sup>, M. Sauer<sup>d</sup>

<sup>a</sup>Institut F.-A. Forel, 10 route de Suisse, CH-1290 Versoix, Switzerland

<sup>b</sup>Fachgebiet Geochemie und Hydrogeologie, Univ. Bremen, 330440 Bremen, Germany

<sup>c</sup>UMR-INRA GeoSol, CST, University of Bourgogne, 6 bd Gabriel, 21000 Dijon, France

<sup>d</sup>Justus Liebig Str. -21 G-28257 Bremen, Germany

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## Abstract

Overbank sediments from the River Weser provide a record of geochemical anomalies which vary distinctively from the regional background as far back as 3500 years BP. The use of Pb isotopes, measured by inductively coupled plasma mass spectrometry (ICP-MS), in combination with the determination of heavy metal concentrations has identified the mining and smelting activities that took place early in the Harz Mountains, as the source of contamination. The regional background was defined from sediments deposited prior to 3500 years BP with Pb and Zn concentrations of about  $23 \pm 7$  and  $109 \pm 38 \mu\text{g g}^{-1}$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of  $1.215 \pm 0.002$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios of  $2.044 \pm 0.002$ . The isotopic characteristics of the Pb in the sediments can be easily explained by a simple two-component mixing model involving: (i) the background component; and (ii) Pb derived from the Harz Mountain ore bodies characterised by  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.167–1.187 and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios of 2.075–2.096.

The rapid determination of isotopic ratios by ICP-MS has advantages over Thermal Ionisation Mass Spectrometry. It enables large-scale investigations in prospecting archaeology or more-recent history. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Pb isotopes; pollution; mining; Harz; overbank sediments

## 1. Introduction

Mining operations are believed to have started in the Harz Mountains during the Bronze Age (Bartels, 1996). From archeometrical analysis of ore and slag it is known that the Harz Mountains have been mined since the 3rd century (Roseneck, 1994). Smelting and mining from the 3rd to the 10th century were observed at several places (Denecke, 1994). At that time, work was carried out using the simplest technologies and pits were dug into the ground to a maximum depth of

about 40 m. Mining of the Rammelsberg ore was fully established by 968 A.D. (Mohr, 1978), and continued until the 14th century. The earliest mining activities of the Upper Harz' hydrothermal Cu–Zn–Pb mineralisation took place during the 13th century (Liessman, 1992). In the 14th century mining fell into a great crisis. The pestilence, the flooded mines and the demand for capital brought the mining near to collapse. In 1445 the mining again became more intensive with the help of new technical methods to trail the water (Hauptmeyer, 1994). After a phase of intensive mining following 1750, the mines were shut down in 1988 after more than 1000 years of industrial activity (Roseneck, 1994). Mining was combined with

\* Corresponding author. Fax: + 33-380396387.

E-mail address: fabrice.monna@u-bourgogne.fr (F. Monna).

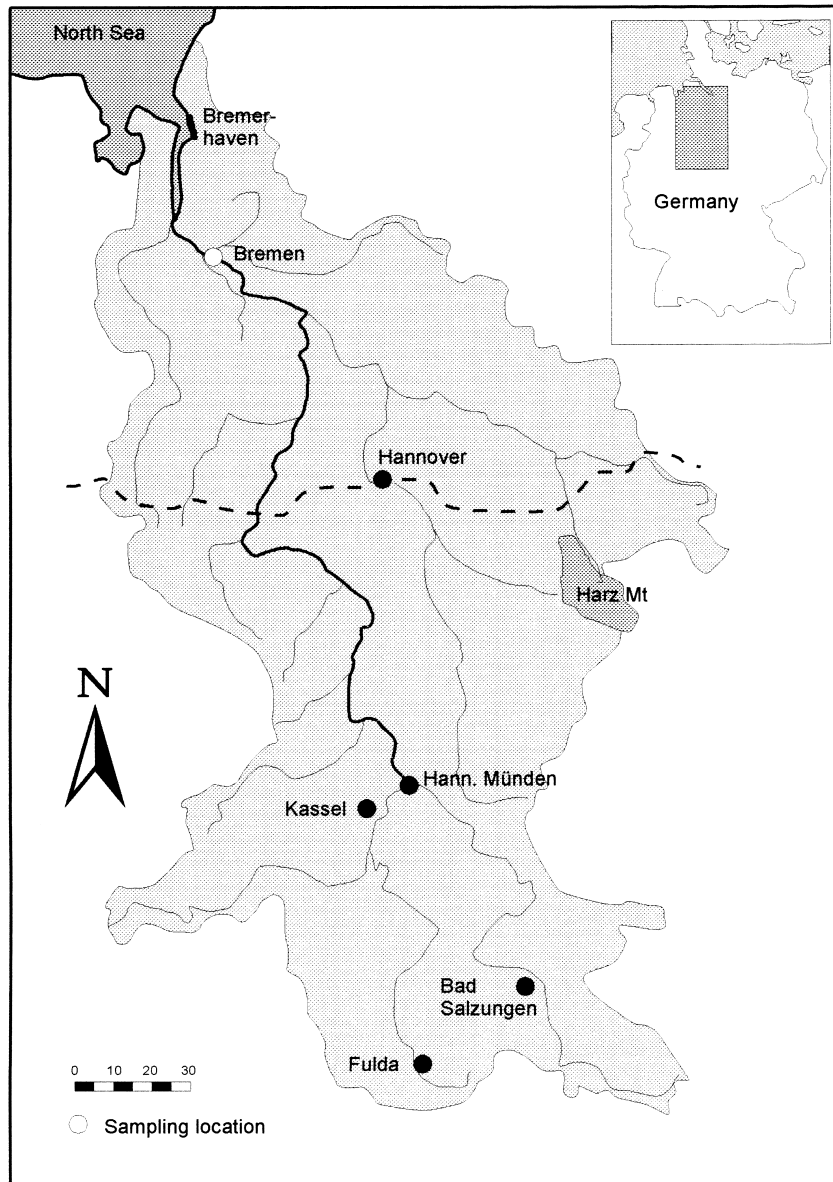


Fig. 1. Map of River Weser watershed and location of sampling.

the intensive usage of the forests in the Harz Mountains. Wood was used to fire the melting furnace, and was the best available construction material and source of energy during industrialisation. As a consequence, increasing erosion led to more transport of eroded matter in the rivers and higher downstream sedimentation.

In 1997, Matschullat et al. (1997) reported

geochemical anomalies in overbank sediments from the Uferbach catchment (Harz Mountain region). These authors interpreted their findings as evidence of four phases of smelting and mining of the hydrothermal deposits of the Upper Harz, which occurred in the medieval (1140–1345 A.D.), karolingian (825–890 A.D.), roman–germanic (425–500 A.D.) and early historic (825–625 B.C.) times. Other geochemical

Table 1  
Overview of the stratigraphic situation of the investigated sediments

Time years BP	Pollen Overbeck (1975)	Cultural periods	Units
500	XII <sub>c</sub>	Modern times	Meadow loam AIV
	XII <sub>b</sub>		
1000	XII <sub>a</sub>	Middle ages	Meadow loam AIII
1500	XI		
2000	X	Iron age	Hiatus
2500			
3000	IX	Bronze age	Meadow loam AII
3500		Neolithic period	Meadow loam AI
4000			
4500			

anomalies were observed by Ortlam (1989); and Sauer (1995) at about 10 km from Bremen, in overbank sediment cores of the River Weser representing approximately 5000 years of deposition. The influence of early Pb mining and smelting in the Harz Mountains was proved to be the source even though the site is more than 200 km from the presumed point source. Pb/Zn ratios supported this hypothesis.

The present study aims to complement this earlier work by using Pb isotope data. The isotopic composition of Pb has been used extensively as an indicator of anthropogenic contribution in many ecosystems, and more particularly to inves-

tigate the impact of recent Pb smelting and/or mining on the surrounding environment (Öhlander et al., 1992; Gulson and Wilson, 1994; Chiaradia et al., 1997; Munksgaard and Parry, 1998). The rationale for this method is abundantly detailed elsewhere (see for instance the Clair C. Patterson Special Issue, 1994. *Geochim. Cosmochim. Acta* 58). Samples of different ages were therefore analysed in overbank sediments of the River Weser for their Pb isotopes in order to define the geogenic background, to confirm or to reject the hypothesis of the influence of mining and smelting activities from the Harz mountains and possibly to determine the contributions of each component.

Table 2

Heavy metal concentrations expressed in  $\mu\text{g g}^{-1}$ , and Pb isotopic compositions in the overbank sediments of River Weser. The errors correspond to the confidence interval at 95%. The symbol # is for replicates

Core	Sample	Depth (m)	Cu ( $\mu\text{g g}^{-1}$ )	Pb ( $\mu\text{g g}^{-1}$ )	Zn ( $\mu\text{g g}^{-1}$ )	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
SB 41	1	IV 0.00–0.20	22 ± 1	52 ± 3	111 ± 4	18.59 ± 0.04	38.66 ± 0.09	1.184 ± 0.001	2.080 ± 0.002
	2	IV 0.20–0.40	48 ± 5	110 ± 3	204 ± 5	18.51 ± 0.02	38.43 ± 0.09	1.186 ± 0.003	2.076 ± 0.004
	#2	–	52 ± 2	117 ± 3	220 ± 8	–	–	–	–
	3	IV 0.40–0.70	54 ± 4	114 ± 3	213 ± 4	18.54 ± 0.04	38.58 ± 0.04	1.187 ± 0.002	2.080 ± 0.005
	#4	–	49 ± 1	112 ± 2	207 ± 4	–	–	–	–
SB 42	1	IV 0.00–0.20	38 ± 2	125 ± 4	203 ± 9	18.59 ± 0.08	38.72 ± 0.14	1.181 ± 0.002	2.083 ± 0.005
	#1	–	39 ± 2	132 ± 3	212 ± 7	–	–	–	–
	2	IV 0.20–0.40	39 ± 2	136 ± 4	191 ± 7	18.57 ± 0.04	38.45 ± 0.15	1.187 ± 0.002	2.071 ± 0.005
	3	IV 0.40–0.80	29 ± 1	46 ± 2	155 ± 2	18.80 ± 0.06	38.91 ± 0.14	1.194 ± 0.001	2.070 ± 0.002
	#3	–	–	–	18.66 ± 0.04	38.52 ± 0.10	1.194 ± 0.002	2.065 ± 0.003	
SB 43	1	IV 0.00–0.20	41 ± 4	133 ± 2	203 ± 17	18.44 ± 0.03	38.36 ± 0.06	1.183 ± 0.002	2.079 ± 0.004
	#1	–	–	–	–	18.49 ± 0.06	38.39 ± 0.11	1.184 ± 0.002	2.076 ± 0.002
	2	IV 0.20–0.40	42 ± 1	133 ± 2	200 ± 9	18.52 ± 0.06	38.43 ± 0.13	1.187 ± 0.002	2.076 ± 0.003
	3	IV 0.40–0.80	44 ± 2	79 ± 1	180 ± 6	18.46 ± 0.05	38.28 ± 0.21	1.189 ± 0.003	2.075 ± 0.006
	#3	–	41 ± 1	73 ± 2	168 ± 6	18.56 ± 0.04	38.49 ± 0.11	1.189 ± 0.002	2.073 ± 0.006
SB 44	1	IV 0.00–0.20	40 ± 2	122 ± 2	220 ± 5	18.62 ± 0.04	38.75 ± 0.08	1.184 ± 0.001	2.081 ± 0.002
	#1	–	–	–	–	18.65 ± 0.05	38.79 ± 0.08	1.185 ± 0.001	2.080 ± 0.002
	2	IV 0.20–0.40	35 ± 3	41 ± 2	163 ± 9	18.87 ± 0.04	38.96 ± 0.06	1.197 ± 0.001	2.066 ± 0.002
	3	IV 0.50–0.90	27 ± 1	22 ± 1	123 ± 1	19.10 ± 0.05	39.21 ± 0.05	1.209 ± 0.001	2.053 ± 0.002
SB 51	1	III 1.20–1.40	61 ± 6	35 ± 2	179 ± 10	18.77 ± 0.06	38.68 ± 0.12	1.202 ± 0.003	2.061 ± 0.007
	2	II 3.20–3.50	64 ± 4	28 ± 1	151 ± 7	18.99 ± 0.05	39.00 ± 0.11	1.209 ± 0.005	2.052 ± 0.007
	3	I 5.20–5.40	24 ± 3	16 ± 1	72 ± 1	19.20 ± 0.05	39.25 ± 0.12	1.217 ± 0.001	2.044 ± 0.003
SB 53	1	III 0.30–0.60	46 ± 2	33 ± 1	139 ± 3	18.68 ± 0.04	38.56 ± 0.09	1.197 ± 0.002	2.065 ± 0.004
	3	I 2.30–2.40	42 ± 3	24 ± 1	137 ± 2	19.03 ± 0.07	38.99 ± 0.08	1.213 ± 0.004	2.046 ± 0.005
SB 54	1	III 0.30–0.60	41 ± 3	36 ± 3	136 ± 7	18.74 ± 0.07	38.52 ± 0.14	1.207 ± 0.002	2.055 ± 0.003
	2	II 1.50–1.80	47 ± 4	32 ± 2	143 ± 8	18.98 ± 0.07	38.89 ± 0.15	1.214 ± 0.003	2.050 ± 0.004
	3	I 2.30–2.40	32 ± 2	28 ± 3	118 ± 6	19.04 ± 0.08	38.88 ± 0.18	1.216 ± 0.003	2.042 ± 0.003

## 2. Site area

River Weser is located in Northern Germany (Fig. 1). With a length of 440 km, its watershed extends over 45 300 km<sup>2</sup> and crosses from the south to the north Hercynian formations surrounding the Harz Mountains, the triassic lower Saxony basin and finally the upper cretaceous basin of North Germany. A sampling campaign was undertaken by Sauer (1995) in overbank sediments of the River Weser, in a rural area located 5 km downstream of the centre of Bremen (Fig. 1). Seventy-two cores were sampled in meadow loams (1–10 m thick) overlying fluvio-glacial deposits from Saalian and Weichselian glaciation (so-called Weser sands). The strategy of coring consisted in a transect of about 2.5 km perpendicular

to River Weser. Grain size analysis indicated a uniform silty texture (more than 50% less than 8  $\mu\text{m}$  and almost nothing greater than 63  $\mu\text{m}$ ). Different colours, related to different concentrations of organic matter and redox conditions, were observed and enabled the characterisation of four units of meadow loams. The youngest level, namely 'IV', is exposed in a band of about 500–600 m along the River Weser. Extending between 0.5 and 1.5 m depth, it consists of brown to reddish-brown silty material coming from a gley-type soil layer ( $G_0$  horizon). Inland, 600 m further along the river, three successive units are recognised in the cores. The top unit 'III' has a relatively constant depth (0.5–1 m). Although comparable to unit 'IV' in its organic carbon and nitrogen contents:  $\sim 2$  and  $\sim 0.2\%$ , respectively, differences

can be noticed in colour (light brown with iron concretions) as well as in the pH ( $\text{CaCl}_2$ ) value (5.2 instead of 5.6 in horizon 'IV'). The underlying level, namely 'II' is easily recognisable by its dark mottled brown colour and high organic carbon and nitrogen contents ( $\sim 10$  and  $\sim 0.7\%$ , respectively). However, it is not continuous. The thickness of the deepest unit 'I' varies widely between 0.5 and 4 m. It is a dark grey formation featuring scattered sand lenses. It presents a decrease in organic carbon and nitrogen ( $\sim 2$  and  $\sim 0.2\%$ , respectively). Different types of trees, bushes, species of grass and corns were identified and counted by pollen analysis. Age determinations were done by Sauer (1995) according to the method of Overbeck (1975): the unit 'IV' was deposited between 500 and 900 years BP, 'III' between 900 and 1500 years BP, 'II' between 3000 and 3500 years BP and finally 'I' between 3500 and 5000 years BP. An overview of the stratigraphic profile and pollen ages is reported in Table 1.

### 3. Methodology

Seven cores among the 72 sampled by Sauer (1995) were analysed for their Pb isotopic compositions. Four different cores belonging to the unit 'IV' (SB 41, SB 42, SB 43 and SB 44) were selected along the transect previously mentioned, at a distance of between 200 and 600 m from the river. Each core was divided into three samples corresponding to the top, the middle and the bottom of the unit. The three remaining cores (SB 51, SB 52 and SB 54) were taken at a distance of approximately 1.5 km from the river. They cross the three units described above: 'I', 'II' and 'III'. One sample was obtained from each unit (cf. Table 2).

Metal concentrations and isotopic measurements were carried out in a class 100–1000 clean lab. Approximately 200 mg of sediments were totally dissolved by using a mixture of 3 ml each of concentrated  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HF}$  (all Merck suprapure quality) in pressured Teflon bombs using a microwave oven (MLS ETHOS) with the following settings: 5 min at 400 W, 2 min at 100 W, 10 min at 600 W and finally 10 min at 700 W (magnetic stirring, pressure max: 20 bar). One blank and one reference material sediment (RMS) were systematically added to each set of seven unknown samples (nine positions

available). After total dissolution, the solutions were evaporated to dryness and were dissolved again in 5 ml of suprapure nitric acid under microwave assistance with the same settings as above. One-third was stored for metal concentration measurements, and two-thirds for Pb isotope analysis. Cu, Pb and Zn concentrations were determined after dilution with MilliQ water by ICP-MS (POEMS 1, Thermo Jarrell Ash Co.) using on-line addition of Rh/Re solution. Blank contributions were always found to be negligible compared to the total amount of heavy metal in the samples. Reference material sediment analyses were at worst always within  $\pm 10\%$  of the expected values. A precision of about 10% was also assessed by replicating three unknown samples (noted “#” in the Table 2).

Prior to isotopic analysis, Pb separation was achieved on AG1X4 resin following the procedure described elsewhere (Monna et al., 1997). The Pb isotopic ratios were measured by quadrupole-based ICP-MS. More details about settings, analytical time management and mass bias correction via NBS 981 measurements can be found in Monna et al. (1998). The signal of 'blank + background' was always less than 0.1% of the total signal and was systematically subtracted. Replicates show that the  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios are reproducible, considering the analytical precision (0.1–0.2% at 95% confidence level). Those including the  $^{204}\text{Pb}$  are also generally reproducible, but a few significant discrepancies may be observed (see the SB 42.1 sample). Only  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios will be discussed here, although other ratios could be used to provide the same interpretations.

### 4. Results

The Pb isotopic compositions and heavy metal concentrations are listed in Table 2. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios range from 1.181 to 1.217, whereas the  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios concomitantly decrease from 2.083 to 2.042. Fig. 2,  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  shows a linear relationship of the two isotope ratios following the age of samples, which suggests a mixing between two (or more) components. The changes in isotope ratios are much greater than the uncertainties in the measurements and are significant in all cases.

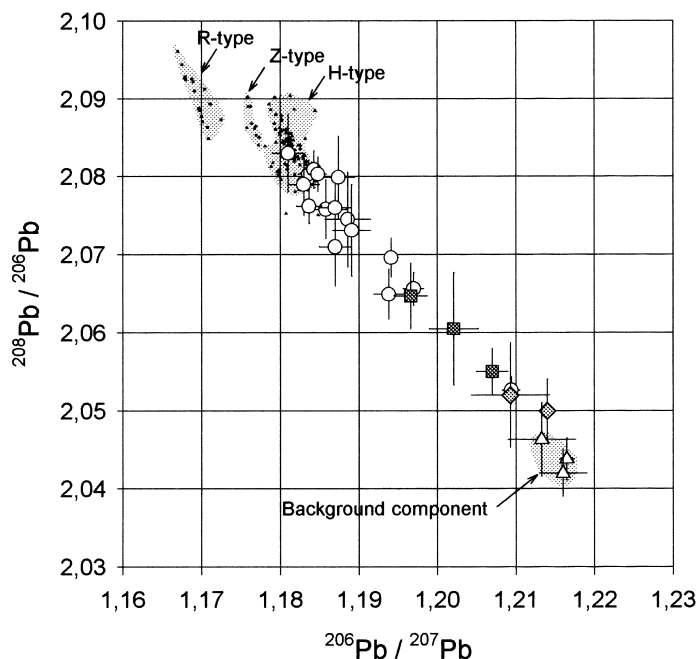


Fig. 2.  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  in overbank sediments deposited at: ( $\Delta$ ) 3500–5000 years BP; ( $\blacklozenge$ ) 3000–3500 years BP; ( $\blacksquare$ ) 900–1500 years BP; and ( $\circ$ ) 500–900 years BP. For a comparative purpose the Pb isotope compositions of Harz' mineralisations have been reported. R-type for syngenetic mineralisation of the Rammelsberg, H-type for hydrothermal veins in the western Harz Mountains and Z-type for lead from minor mineralisation in the Zechstein karst (Lévêque and Haack, 1993).

In more detail, the oldest unit, 'I', deposited between 3500 and 5000 years BP (samples SB 51.3, SB 53.3 and SB 54.3), exhibits the highest  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios (1.213–1.217, average: 1.215) and the lowest Pb and Zn concentrations (average: 23 and  $109 \mu\text{g g}^{-1}$ , respectively). Unit 'II' (samples SB 51.2 and SB 52.2; 3000–3500 BP) is characterised by slightly lower radiogenic Pb isotope compositions and higher Pb and Zn concentrations. This tendency is accentuated in the unit 'III' (samples SB 51.1, SB 53.1 and SB 54.1; 900–1500 BP) and then in unit 'IV' (samples from the cores SB 41, SB 42, SB 43 and SB 44; 500–900 BP). Despite the low-resolution sampling, it can be seen that the Pb and Zn concentrations generally increase from the bottom to the top in the SB 4x cores, whereas the Pb isotopic compositions systematically become less radiogenic.

## 5. Discussion

The wide variations of Pb concentrations observed

in the sedimentary columns, and more particularly the notable increase after 1500 BP, cannot be explained solely by a simple variation of background or by an upward interstitial transport of lead. Indeed, the concentration shifts occurred with concomitant changes in Pb isotopic signatures, which necessarily implies at least two distinct sources: one is the background lead (native geochemical lead) and the other(s) is less radiogenic and may have an anthropogenic origin.

The establishment of a simple mixing model requires the precise characterisation of the regional 'background' end-member as the first source involved. Usually, it is assessed using sediments deposited in pre-industrial times (i.e. 200 or 300 years ago). This notion has a different meaning because the introduction of a contaminated component presumably began as early as 3500 years ago. It is, however, reasonable to assume that unit 'I' (3500–5000 years BP) was virtually free from human influence. This should represent a regional average of all the Pb present in rocks and soils of the River Weser

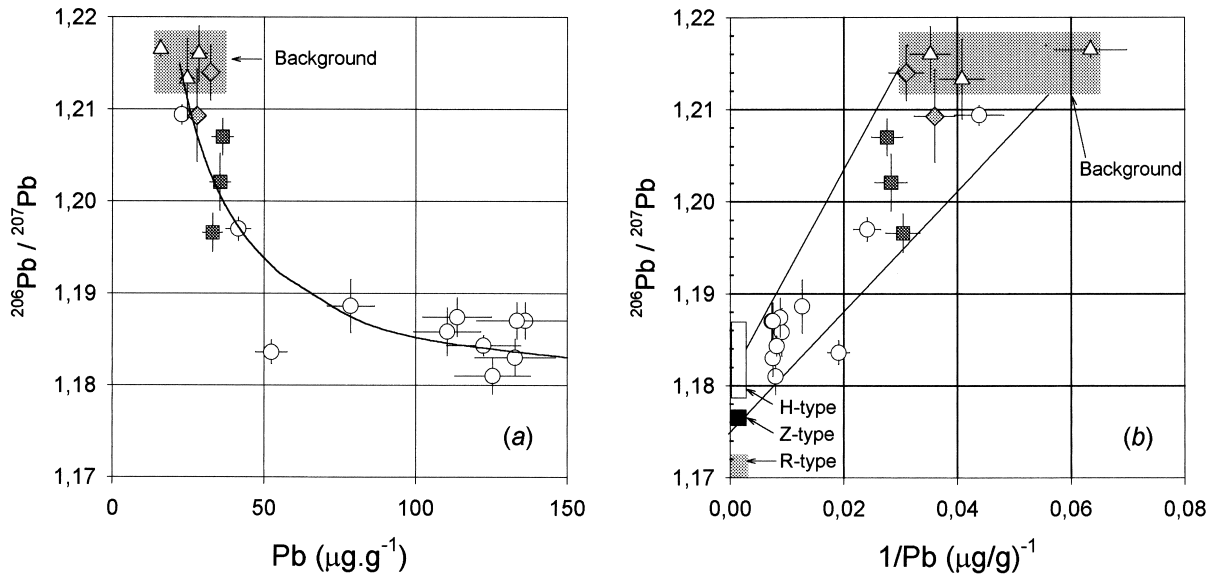


Fig. 3. (a)  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $\text{Pb}$  (in  $\mu\text{g g}^{-1}$ ) diagram. The hyperbolic curve is constructed from binary mixing between a background component ( $\text{Pb} = 22 \mu\text{g g}^{-1}$ ,  $^{206}\text{Pb}/^{207}\text{Pb} = 1.215$ ) and a contamination source characterised by  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.177. (b):  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $1/\text{Pb}$  ( $\mu\text{g/g}$ ) $^{-1}$  diagram. ( $\Delta$ ) 3500–5000 years BP, ( $\blacklozenge$ ) 3000–3500 years BP, ( $\blacksquare$ ) 900–1500 years BP and ( $\circ$ ) 500–900 years BP. The fields of Pb mineralisation are reported for comparative purposes (Lévêque and Haack, 1993).

watershed, including the Pb, which derives naturally from the major Pb ore deposits. But the influence of this later should be reduced, since at that time the mineralisation had not been exploited and could not naturally be a major source of contamination because of their distance and their feature (mainly vein-type deposits). Pb isotopic compositions are homogeneous in the horizon of unit 'I' ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.215$ ) indicating a steady origin. Such a signature is in good agreement with those considered as representative of the average upper continental crust (Kramers and Tolstikhin, 1997). The large Pb concentration variations (16 and  $28 \mu\text{g g}^{-1}$ ) might thus be due to small changes in grain size or modifications of the depositional conditions, and not a result of changes in origin.

It is now well known that the environment has been affected by global changes in the early stages of human history. In ancient times, Pb was produced in open-air furnaces, and obviously, no controls of atmospheric emission rates or wastewater quality were carried out. For instance, 'Paleo'-pollution has been clearly identified in peat bogs from the Jura Mountains (Shotyk et al., 1998). There, the presence of anthropogenic-derived lead was noticed as early as 3000 years BP, and was explained as the historical

record of ancient mining and long-range transport of aerosols from the intensively mined Iberian Peninsula. Similarly, Hong et al. (1994) documented the atmospheric deposition of Pb in Greenland from an ice core covering the period 3000–500 years ago. Pb concentrations started to increase from 2500 years BP and remained high during an 800 year period, resulting from the long-range atmospheric transport of Pb coming from ore bodies intensively mined during Greco-Roman times (Spain, Britain, Balkans, Greece and Asia Minor). Another period of intense activity was also noticed 1500–500 years ago during Medieval and Renaissance times.

For our overbank sediments the situation was slightly different because the long-range atmospheric transport should have had a very minor importance compared to the direct fluvial sources. The contribution from lithogenic material was much more important in the overbank sediments than in ice and peat bogs, and it is doubtful that atmospheric inputs were high enough to be recognised. Indisputable sources of Pb contamination are mining and smelting activities that took place early in the Harz Mountains. It is necessary to test the coherence of this hypothesis with the Pb isotopic

Table 3

Pb isotopic compositions of Harz' mineralisation (Lévêque and Haack, 1993), R-type for syngenetic mineralisation of the Rammelsberg (SEDEX sedimentary exhalative deposit), H-type for hydrothermal veins in the western Harz Mountains and Z-type for lead from minor mineralisation in the Zechstein karst. Actually, these groups are probably even more homogeneous than it appears above. About two-thirds of the variation within the cluster may be simply explained by isotopic fractionation in the mass spectrometer

Harz' mineralisation	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
R-type	18.242–18.311	38.087–38.312	1.1670–1.1725	2.0849–2.0961
Z-type	18.356–18.422	38.259–38.505	1.1758–1.1772	2.0841–2.0902
H-type	18.434–18.564	38.354–38.679	1.1786–1.1867	2.0751–2.0904

composition changes that are observed in the sedimentary column.

As depicted in a diagram  $^{206}\text{Pb}/^{207}\text{Pb} = f(\text{Pb})$ , our data roughly define a hyperbolic curve (Fig. 3a), which can be basically treated as a two-component mixture following the conventional law (Faure, 1986):

$$\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_m \approx \frac{\text{Pb}_A \text{Pb}_B \left[ \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_B - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_A \right]}{\text{Pb}_m (\text{Pb}_A - \text{Pb}_B)} + \frac{\text{Pb}_A \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_A - \text{Pb}_B \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_B}{\text{Pb}_A - \text{Pb}_B} \quad (1)$$

where  $(^{206}\text{Pb}/^{207}\text{Pb})_i$  and  $\text{Pb}_i$  for  $i = m, A$  and  $B$  are the isotopic composition and the Pb concentrations of the mixture, the component A and the component B, respectively. In the present case, the first obvious component is the regional background. If the pollutant component derives from the mining or smelting of Pb, one can reasonably consider that the waste exhausts, originally rejected in the fluvial network, were much more concentrated than the natural background ( $\text{Pb}_{\text{Anthr.}} \gg \text{Pb}_{\text{Back.}}$ ). This leads to the following simplification:

$$\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_m \approx \frac{\text{Pb}_{\text{Back.}} \left[ \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{Back.}} - \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{Anthr.}} \right]}{\text{Pb}_m} + \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{Anthr.}} \quad (2)$$

This mixing hyperbola model can be transformed into a straight line by plotting  $(^{206}\text{Pb}/^{207}\text{Pb})_m$  vs.  $1/\text{Pb}$ . The intercept at the Y-axis should then represent the isotopic composition of the source of contamination. Actually, Harz' mineralisation does not present a uniform Pb isotopic composition, but rather plots into three very restricted clusters in Pb–Pb diagrams, corresponding to Devonian, presumed Permian and Mesozoic mineralisation periods (Figs. 2 and 3b; Table 3; Lévêque and Haack, 1993). This mineralisation was interpreted as deriving from a uniform crustal source of Pb, which was either extracted at three different times, or was homogenised during these extraction processes (Lévêque and Haack, 1993). Our data fit well with this simple binary mixing model, and all the samples can be explained as resulting from a variable contamination by a Pb originating from Harz' mineralisation (Fig. 3b). The position of the samples on the mixing field also strongly suggests that the contaminated Pb mainly derived from the H- and/or Z-type mineralisation rather than from the Rammelsberg sedimentary-type (R-type). This is not surprising because many important mineralisations belong to the most radiogenic hydrothermal vein group (H-/Z-type), well spread over this geological area. Mining history also indicates early activity on these vein-type deposits due to their accessibility. Moreover, the R-type deposit only occurs on a very restricted area and was mainly exploited later during industrial times. So, by taking basically a background signature with  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.215, and a Pb with  $^{206}\text{Pb}/^{207}\text{Pb} = 1.180$ , typical of the Harz Pb ore bodies, one can calculate that the anthropogenic contribution represents 3–16% of total Pb buried in the samples of unit 'II', 23–53% in unit 'III' and 52–97% in unit 'IV' (if we exclude the sample SB44/1.3 with only 16%).



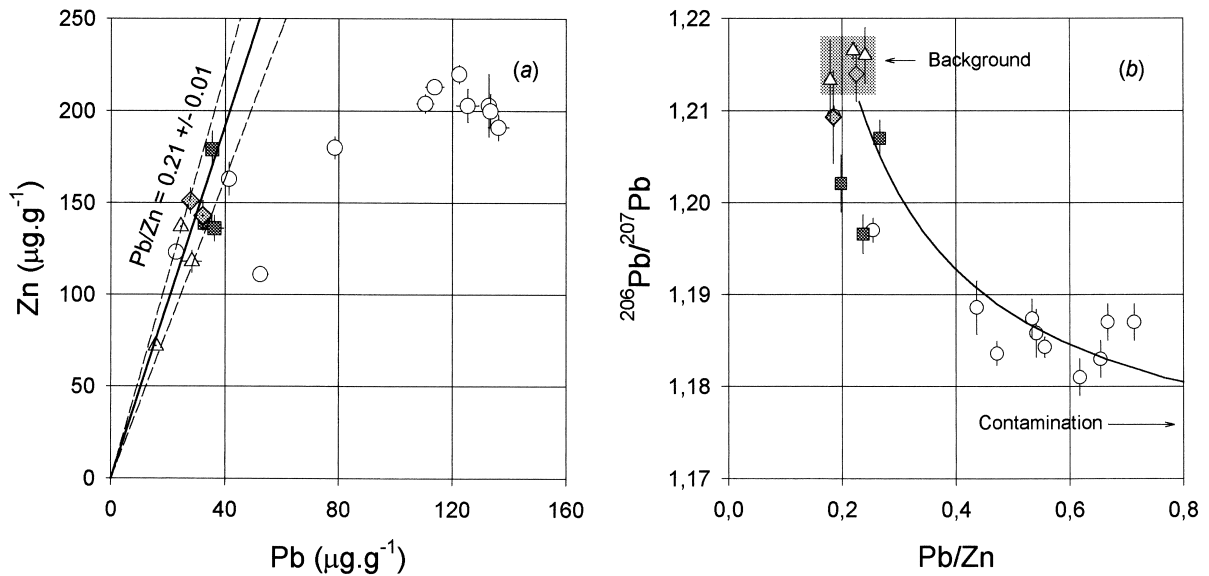


Fig. 4. (a) Pb vs. Zn diagram (both in  $\mu\text{g}\cdot\text{g}^{-1}$ ). (b)  $^{206}\text{Pb}/^{207}\text{Pb}$  vs. Pb/Zn diagram. The hyperbolic curve is constructed from binary mixing between a background component ( $\text{Pb/Zn} = 0.21$ ,  $^{206}\text{Pb}/^{207}\text{Pb} = 1.215$ ) and a contamination source characterised by a Pb/Zn ratio of 1 and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of 1.177. ( $\Delta$ ) 3500–5000 years BP, ( $\blacklozenge$ ) 3000–3500 years BP, ( $\blacksquare$ ) 900–1500 years BP and ( $\circ$ ) 500–900 years BP.

Another clue is given by the Pb–Zn relationship. Plotted on a diagram  $\text{Zn} = f(\text{Pb})$ , the data from the oldest units ('I' and 'II') almost lie on a line passing through the origin with a slope producing a Pb/Zn ratio of  $0.21 \pm 0.01$  (Fig. 4a). Such a value is quite usual for unpolluted sediments, and suggests that, in the deepest horizons, these elements mainly derive from a unique detrital source. In the upper contaminated levels (i.e. unit 'IV'), the Pb/Zn ratio increases to 0.6–0.7, probably because they are contaminated by a Pb-enriched source.

As reported in Fig. 4, the data are in line with a binary mixing model where the Pb/Zn of the anthropogenic source is greater than one. However, it has to be kept in mind that the use of the Pb/Zn ratios for determining the contamination is delicate and presents some limitations, since this ratio is composed of two elements that potentially may have anthropogenic origins. For example, samples from units 'II' and 'III' cannot be suspected to be contaminated looking at their Pb/Zn ratios. In fact, their Pb isotope abundance illustrates a slight contamination by Harz component(s) (see Fig. 3).

## 6. Conclusions

Pollution from smelting and mining activities in the Harz Mountains has been shown by analysis of overbank sediments of River Weser. This influence started as early as 3500 years BP. It has been indicated by Pb and Zn concentrations, and very clearly using stable Pb isotope compositions. The latter tool is much more sensitive than the elemental concentrations when anthropogenic contribution is low, whereas when anthropogenic Pb dominates, the Pb isotope ratios tend to be uniform and concentrations become the best tracer. Because of this sensitivity, geological sources such as ore deposits can be detected even if they do not play a predominant role. However, the precise Pb isotopic characterisation of potential sources is required for the interpretation of mixing curves with the natural background. Combined with high sampling resolution and reliable dating of marine, lacustrine or fluvial sediments, rapid and precise measurements by quadrupole-based ICP-MS therefore offer new possibilities in archaeological/historical studies for the recognition of precursor human impact on the environment.

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