HISTORICAL VARIATIONS IN LEAD FLUXES IN THE PYRENEES (NORTHEAST SPAIN) FROM A DATED LAKE SEDIMENT CORE

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Abstract. Variations in Pb concentration in lake sediments reflect changes in the fluxes of this element in the past. A sediment core from a lake in the Pyrenees (Lake Redó at 2,240 m a.s.l., NE Spain) was studied, with the aim of reconstructing past environmental and climatic conditions in the lake and its catchment area. The core was dated using both ²¹⁰Pb and ¹⁴C. A surface peak of Pb concentration, which was about 10 times higher than the background level, was found. This peak is attributed to mining activities since the beginning of this century. Although Pb pollution due to the combustion of gasoline is expected to be present, no evidence can be deduced from Pb isotope ratios of sediment due to the masking effect of Pb from mines. A second peak appeared in a deeper layer, with a maximum Pb concentration of about 17 times higher than the background level. The origin of this peak is unclear. All evidence suggests that the ancient peak is due to mining operations in the central Pyrenees area, which were not documented historically.

Keywords: Lake Redó, lake sediments, lead, metal pollution, mining, ²¹⁰Pb-dating, Pyrenees, stable Pb isotopes

1. Introduction

Peak concentrations of Pb attributable to contemporary sources commonly are found in surface or near-surface sediments of lakes all over the world (Petit *et al.*, 1984; Davis and Galloway, 1993; Renberg *et al.*, 1994; Ritson *et al.*, 1994; Gobeil *et al.*, 1995). This Pb mainly comes from industrial pollution and from the combustion of leaded gasoline. In countries where unleaded gasoline was introduced in the late 1960s, a decline in Pb content in the sedimentary record has been reported (Moor *et al.*, 1996). In most of these studies, it is also common to find a Pb concentration rise in sediments starting two millennia ago, owing to mining and smelting activities during ancient Greek and Roman times first, and during Medieval and Renaissance times later (Nriagu, 1996). Evidence of northern hemisphere pollution spread from these ancient industries has been found in ice cores from Greenland (Hong *et al.*, 1994).

What had not been found up to now (to our knowledge) is a profile showing a pre-industrial peak of Pb concentration in sediments higher than the modern peak. This finding is even more surprising if we consider that Lake Redó (where we recorded such a profile) is a relatively remote, pristine, high mountain lake. The aim of this paper is to discuss the most probable origin of the Pb fluxes in the lake, in particular that causing the ancient concentration peak.

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2. Methods

2.1. STUDY SITE

Lake Redó is located in the central Pyrenees (42° 38' 33" N, 0° 46' 13" E) at 2,240 m a.s.l. The lake has a surface area of 24 ha, a maximum depth of 73 m, and a mean depth of 32 m. The average water residence time is more than 4 yr. Its catchment area is a small granodiorite basin (155 ha). More than 50 % of the catchment area is composed of bare rock. Soils are generally less than 30 cm deep, and vegetation consists of high mountain grasslands. More details on the physical features and chemistry of Lake Redó may be found in Catalan (1989, 1992).

2.2. SAMPLING

A sediment core was taken from the deepest part of the lake by means of a gravity corer in August 1994. The core was extruded immediately and sliced in 3 mm sections. A subsample was stored in polyethylene bags for ^{210}Pb dating, and another subsample for diverse chemical analyses was kept deep frozen in a polypropylene vial. A soil core was sampled in Lake Redó's-catchment area in July 1995. The soil core was 30 cm deep and was sliced every 5 cm for the determination of total Pb content, stable Pb isotope ratio, and ^{210}Pb content. Galena samples were collected at the Cierco mines, situated further down the valley where Lake Redó is situated, and were analyzed for their stable Pb isotope ratio. Preparation of sediment and soil samples for chemical and isotopic ratio analyses consisted of drying in the oven at 90 °C, followed by grinding in an agate mortar. Samples for ^{210}Pb dating were dried at 45 °C.

2.3. CHEMICAL ANALYSES

A sequential extraction procedure was applied to sediments to partition their components into six operationally defined fractions. Although these fractions are not clearly associated with specific geochemical phases (Kheboian and Bauer, 1987; Gobeil *et al.*, 1995), the procedure leaches progressively less labile chemical species. The phases indicated below are assumed to be the main contributors to each fraction, but this assignments must be accepted with caution. About 200 mg of dry sediment were distributed in polypropylene assay tubes and extracted sequentially with: 1) 2 mL of 1 M ammonium acetate (pH 7) - this step leaches mainly soluble and exchangeable forms; 2) 2 mL of 1 M ammonium acetate acidified to pH 5 with acetic acid - carbonates are dissolved in this step; 3) 5 mL of 0.04 M hydroxylamine hydrochloride in 2.5% acetic acid at 96 °C - mostly Fe and Mn oxides are leached; 4) 2 mL of 1.4 M ammonium acetate in 9% HNO_3 , after digestion with 1.6 mL of H_2O_2 at 85 °C - organic matter is digested in this step; 5) 8 mL 0.2 M NaOH at 95 °C - biogenic Si, mainly opal from diatom frustules, is dissolved. This procedure was adapted from Tessier *et al.* (1979), with an additional step to extract biogenic Si taken from Engstrom and Wright (1984).

All samples were analyzed by inductively coupled plasma spectrography for major elements and trace metals in a PolyScan 61E Thermo Jarrell Ash instrument. Nine procedure blanks were performed (Table I).

2.4. DATING

^{210}Pb was determined in each section of the top 8 cm of the profile through determination of its daughter ^{210}Po in equilibrium. The samples were digested in a microwave oven in a $\text{HNO}_3\text{:HCl:HF:H}_2\text{O}$ mixture (5:2:3:10 mL). Then, 25 mL of boric acid was added to convert the excess fluorides into tetrafluoroborates by heating. The resulting solutions were evaporated until they were almost dry and the residual was dissolved in 1 M HCl. Polonium isotopes spontaneously deposited onto silver disks at 60–70 °C for 8 hr while being stirred (Sanchez-Cabeza *et al.*, in press). Polonium isotopes were counted on alpha spectrometers equipped with low background SSB detectors (EG&G Ortec Model SSB 450 R). Excess ^{210}Pb for each section was calculated by subtracting the supported fraction, in equilibrium with ^{226}Ra , from the total ^{210}Pb . Supported ^{210}Pb , namely $58.0 \pm 1.3 \text{ Bq kg}^{-1}$, was estimated from the mean value of seven deep sections where excess ^{210}Pb was not present. ^{210}Pb dating was achieved by application of the Constant Rate of Supply (CRS) model (Appleby and Oldfield 1978) in a modified version (Minimum Variance, CRS/MV, Tobin and Schell, 1988; Sanchez-Cabeza *et al.*, 1994).

^{14}C dating was performed by Beta Analytic Inc. on 12 bulk sediment samples, using their standard method. ^{14}C was measured in an accelerator-mass-spectrometer. The Pretoria calibration procedure was used for date calibrations (Vogel *et al.*, 1993).

TABLE I

Pb concentration in the five extractable fractions and the acid extraction and isotopic ratios in the acid extraction and the galena minerals. The extractions used for total Pb (sequential extraction: sum of fractions 1 to 5 which accounts for biogenic silica, and sum of fractions 1 to 4 without biogenic silica) and for Pb isotope ratio analyses ($\text{H}_2\text{O}_2\text{-HNO}_3$ extraction) are compared (differences are expressed as a percentage).

Depth (mm)	Concentration in fraction (mg kg^{-1})								Isotopic ratios		
	1	2	3	4	5	S 1-4	S 1-5	acid extr.	% diff.	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
6	11	86	141	51	26	290	316	298	5.7	1.172 ± 0.0023	2.095 ± 0.0029
45	2	11	21	16	10	50	60	45	25.0	1.198 ± 0.0019	2.064 ± 0.0033
69	3	15	38	26	12	82	94	64	31.9	1.185 ± 0.0021	2.078 ± 0.0037
98	0	10	22	22	11	54	64	60	6.3	1.188 ± 0.0014	2.084 ± 0.0041
142	15	138	223	111	28	487	514	495	3.7	1.173 ± 0.0023	2.099 ± 0.0031
201	0	3	15	9	5	27	32	18	43.7	1.217 ± 0.0024	2.048 ± 0.0042
299	0	0	16	13	7	29	36	17	59.4	1.224 ± 0.0019	2.038 ± 0.0036
anks	1 ± 1	1 ± 1	0 ± 0	1 ± 1	1 ± 1			1 ± 1			
Bossost-Liat galena *										1.152	2.117
Cierco galena										1.179 ± 0.0015	2.093 ± 0.0040

* From Cardellach *et al.* in press (analytical errors not reported)

2.5. LEAD ISOTOPE RATIO ANALYSIS

About 50 mg each from the sediment and soil samples were subjected to medium-pressure microwave digestion (5 min at 250 W, 8 min at 600 W, 7 min at 350 W) with 4 mL 65 % HNO_3 and 1 mL 30 % H_2O_2 . The same procedure was followed for 4 blanks. After digestion, the samples were filtered to remove the insoluble fraction and diluted. From the galena sample, 30 mg were dissolved in 10 mL of hot 65 % HNO_3 and diluted. Lead isotope ratios as well as Pb concentrations were measured in these solutions with a Perkin Elmer Sciex Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS). The accuracy of concentration determinations was checked by digesting and analyzing NIST standard reference material 2704 (Buffalo River sediment). After blank subtraction and correction of the Pb signals for dead time losses, the measured Pb isotope ratios were corrected for instrumental mass discrimination by measuring a standard solution of NIST standard reference material SRM981 (common Pb isotopic standard). The accuracy of the Pb isotope ratio determinations was checked by measuring Pb isotope ratios in SRM981. The experimentally determined concentration and isotope ratios in the standard reference material corresponded to the certified ratio within the experimental uncertainty.

3. Results

The time scale relative to depth, established by combining ^{210}Pb and ^{14}C data, is shown in Figure 1. Radiocarbon dates resulted in a time scale shifted by 940 ± 40 yr BP, the apparent age of the surface sediment sample. Consequently, all radiocarbon dates were corrected by subtracting the apparent surface age. This agreed closely with the ^{210}Pb dating: the core sample from 18 mm depth was estimated to be from 1904 (± 2 yr) by the ^{210}Pb method, and from 1905 (± 150 yr) by the ^{14}C method. Estimated sedimentation rates changed with depth: from surface to 30 mm it was on average 0.23 mm yr^{-1} (spanning 1875 AD - 1994 AD), with two periods of higher sedimentation rates identified during the first half of the twentieth century (Ani-Ragolta, 1996); from 30 to 171 mm sedimentation was 0.08 mm yr^{-1} (394 AD - 1875 AD), and from 171 to 458 mm it was 0.03 mm yr^{-1} (8171 BC - 394 AD). These rates were estimated by linear fitting of depth against the age of ten, four and five dated samples, respectively. They were fairly constant within each period, with the exception of the two episodes during the twentieth century.

The Pb concentration profile in Lake Redó is displayed in Figure 1. Concentrations shown in the graph are the sum of fractions 1-5, hereafter referred to as total extractable Pb. Atmospheric Pb of anthropogenic origin is assumed to be within these fractions. The total extractable Pb values obtained with the sequential extraction procedure correlate with those obtained with the acid extraction method used for isotope ratio determination (Table I). The higher concentrations in sequentially extracted samples are attributable to the fact that this procedure includes a final step that releases the biogenic Si. This biogenic Si fraction is seldom considered when analyzing extractable Pb and other trace metals, but it may contain these elements. Therefore, the Pb concentrations from the acid extraction used for isotope analysis is closer to the sum of fractions 1-4, which were also extracted in acid media. We assume that the isotope ratios measured correspond to the Pb in fractions 1-4. We do not expect the isotope ratios of the total extractable Pb to be significantly

Fig. 1. Lead concentration profiles in sediments: total extractable Pb and natural Pb (as estimated from Al concentrations) profiles, and the ²⁰⁶Pb/²⁰⁷Pb ratio at certain levels are plotted against the depth and time scales obtained by ²¹⁰Pb and ¹⁴C dating.

different from those we have measured because the Pb not leached in the acid extraction is a small amount. On the other hand, although some authors have found differences in the Pb isotope composition between the organic and mineral fractions in soils (Erel and Patterson, 1994), such differences between different lake sediment fractions other than the mineral residue (which was not considered in this study), have not been found in other studies (Gobeil *et al.*, 1995).

Background concentrations of total extractable Pb in the deeper part (below 200 mm) of the core were 20–30 mg kg⁻¹. In the upper part of the core, Pb concentration became higher, with two outstanding peaks at the surface (316 mg kg⁻¹) and at 142 mm depth (514 mg kg⁻¹). A third peak of lower concentration (94 mg kg⁻¹) appeared between 50 and 70 mm. The dating shows that the deepest peak started to rise rapidly at about 467 AD, reached its maximum at 658 AD and declined again to background levels at 1105 AD. This coincides with the period in which worldwide Pb production was lower after the eclipse of the Roman Empire and before the discovery of the Pb and Ag mines in central Europe, according to the widely accepted reconstruction of Settle and Patterson (1980).

Anomalously high Pb contents in the granite rocks, as caused for instance by inclusions of Pb and other metal deposits of hydrothermal origin (Johnson *et al.*, 1996), have been

described in this area of the Pyrenees. To rule out the possibility that increased weathering of these minerals within the catchment area during this period might cause natural accumulation of Pb in sediments, we compared the Pb/Al and Pb/Ba ratios along the profile. Lead, Al and Ba are closely associated in the mineral composition of Pyrenean granites (J. Tritlla, pers. comm.), and one would expect their ratios to remain constant despite changes in weathering rates. Both ratios (as well as the Pb concentration) were on average much lower and more constant in the section of the core between 200 and 300 mm ($\text{Pb/Al} = 10.5 \pm 2.4 \times 10^{-4}$; $\text{Pb/Ba} = 20.9 \pm 5.6 \times 10^{-2}$) than in the upper section ($\text{Pb/Al} = 46.6 \pm 34.3 \times 10^{-4}$; $\text{Pb/Ba} = 87.3 \pm 66.3 \times 10^{-2}$). We thus considered that the values for the ratios in sediments deeper than 200 mm were those of the weathered mineral, and the natural contribution of Pb from the weathering of rocks in the catchment area for the entire core was reconstructed by multiplying the Al and Ba concentrations in sediments by the respective ratios. The reconstructed profiles were practically the same using either Al or Ba. Although Al and Ba could be also pollutants, the variations in concentration with depth did not follow that of Pb, and the possible contamination had a negligible effect on the calculations: the estimated natural Pb concentration was all through the core practically constant and identical to the background levels measured.

Figure 1 shows the natural Pb concentration as estimated from Al, compared to the total extractable Pb concentration. The difference between the two profiles indicated Pb enrichment, which can only be attributed to the contribution from anthropogenic sources through atmospheric deposition. In our core, the Pb excess started to rise in about 674 BC, which corresponded with the rise of Pb concentration in Greenland ice (Hong *et al.*, 1994) and the introduction of coinage (Settle and Patterson, 1980). The modern Pb peak started in about 1900 AD. Although Pb pollution caused by the combustion of leaded gasoline also must contribute to this peak, it is basically a record of the mining activities (Table II) in the nearby northern areas of Bossost and Liat and the southern area of Cierco. Opening of the mines at the beginning of this century (Johnson *et al.*, 1996; Cardellach *et al.*, in press) caused the yearly increase percentage of Pb rise. Between about 1943 and 1963, the period of Spanish post-war industrial development in which both northern and southern

TABLE II

Lead increase rates related to mining activities. The total increase rate was obtained by calculating the increase between two consecutive sediment samples (3 mm slices). The yearly rate is an average for the period between samples, and resulted from dividing the total rate by the number of years in each period.

Period		Pb increase rate (%)		Mining activities
start	end	total	yearly	
1984	1994	6.1	0.6	
1963	1984	30.7	1.5	In 1981, Cierco mines closed
1943	1963	46.6	2.3	During the 1950's, Liat and Bossost mines closed
1932	1943	17.9	1.6	
1916	1932	26.7	1.7	In 1930, Cierco mines opened
1905	1916	19.9	1.8	
1900	1905	8.3	1.7	At beginning of century, mines in Bossost and Liat opened
1889	1900	4.9	0.4	

mines were exploited, the Pb increase rate reached its maximum. Between about 1963 and 1984 only the Cierco mines remained open, causing a lower Pb increase rate, which reached again a minimum after the closure of the last mines in 1981.

Fig. 2. Total extractable Pb content, unsupported ²¹⁰Pb and Pb isotope ratios from a soil core from the Lake Redó catchment.

Measurements from the soil core are shown in Figure 2. The unsupported ²¹⁰Pb measurements showed that all Pb deposited during the last 100 years was in the upper 5 cm. However, the isotopic composition indicated three different origins of Pb (Figure 3): in the 0-5 cm layer, the isotopic ratios were similar to those of surface sediments; in the 5-20 cm layer the isotopic composition resembled that of the ancient peak; and between 20 and 30 cm it was similar to that of the Cierco galena. Similarly, the total extractable Pb concentration changed in these three layers: 100 mg kg⁻¹ (0-5 cm), 30-50 mg kg⁻¹ (5-20 cm), and 20 mg kg⁻¹ (20-30 cm). There is discrepancy between the isotopic composition of Pb in the bottom soil layer and in the background sediment. There are two possible explanations for this: first, the bottom soil layer might contain Pb from another source in the catchment which has no effect in the sediments; second, some Pb might have migrated from the more polluted upper layers towards the bottom, changing the average ratios.

4. Discussion

The only reasonable explanation for the ancient Pb peak is mining and smelting. The Pb isotope composition of sediment samples supports this hypothesis. Table I and Figure 1 show the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in several samples along the sediment core. The background $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, obtained from the 299 mm sample, was 1.224. This figure agrees closely with the mean isotopic composition of pre-industrial sediments over Europe ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.21$; Grousset *et al.* 1994). This ratio decreased slightly at 201 mm, coinciding with the first appearance of excess Pb, and fell dramatically at the ancient peak. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the modern peak was practically the same as the ancient one, and during the period between peaks this ratio increased but remained below the background value. The great similarity of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the two largest peaks strongly suggests a similar origin. The origin of Pb added to gasoline in Europe has been low radiogenic Precambrian ores, mostly the Broken Hill ores (Australia), with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ≈ 1.04 (Grousset *et al.* 1994). The fact that the isotope ratio of both modern and ancient peak was so similar, and well above that of gasoline Pb indicates that the proportion of gasoline Pb in the modern peak must be relatively low (see the reconstruction of anthropogenic Pb isotope ratios below).

To compare the isotopic composition of sediments with the possible sources of pollutant Pb, Figure 3 shows the $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of sediments, soil from the Lake Redó catchment area, and galenas from the Bossost-Liat (Cardellach *et al.* in press) and Cierco mines. The effect of Pb coming from the mines on the isotopic ratios of both ancient and modern peaks could be clearly seen: their composition is a mixture of background sediment Pb and galena Pb.

The final Pb isotope composition of a sediment sample is a result of the proportions in which both natural Pb and anthropogenic Pb are mixed. Equation (1) describes this:

$$\frac{(^{206}\text{Pb}/^{207}\text{Pb})_N \times [\text{Pb}]_N + (^{206}\text{Pb}/^{207}\text{Pb})_A \times [\text{Pb}]_A}{[\text{Pb}]_N + [\text{Pb}]_A} = (^{206}\text{Pb}/^{207}\text{Pb})_T \quad (1)$$

where the subscript *N* denotes the natural fraction, *A* the anthropogenic fraction, and *T* the total. The same equation may be written for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio. In these equations the only unknown variables were the anthropogenic ratios. We assumed the natural fraction ratios to be those of the background sample, whereas the total ratios were those measured for each sample. The natural Pb concentration was estimated from the Pb/Al ratio, and the anthropogenic Pb was the difference between the measured values and the estimates of natural Pb, as discussed above. The equations were solved to find the anthropogenic Pb isotope ratios in our samples (Table III).

Despite the variable total extractable Pb concentrations, the ratios for the anthropogenic fraction were practically the same in both modern and ancient peaks, clearly indicating the effects of mining activities on the composition of pollutant Pb. The similarity between the estimated anthropogenic Pb isotope ratios is remarkable, because one would expect lower values in the surface peak owing to the widespread leaded gasoline contribution. Such coincidence indicated that the proportion of Pb from gasoline in the surface peak is low.

Fig. 3. $^{206}\text{Pb}/^{207}\text{Pb}$ plotted against $^{208}\text{Pb}/^{206}\text{Pb}$ for sediment, soil, and galena samples from Cierco and Bossost-Liat mines.

TABLE III
Reconstructed isotope ratios of anthropogenic Pb.

Depth (mm)	Calibrated date	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
3	1970 AD	1.166 ± 0.0028	2.102 ± 0.0037
45	1706 AD	1.182 ± 0.0040	2.080 ± 0.0073
69	1451 AD	1.165 ± 0.0041	2.099 ± 0.0074
98	1143 AD	1.166 ± 0.0034	2.111 ± 0.0087
142	674 AD	1.169 ± 0.0026	2.103 ± 0.0035
201	659 BC	1.197 ± 0.0140	2.077 ± 0.0251

The samples from 69 and 98 mm showed an anthropogenic Pb composition identical to that of the mining peaks. If it indicates mining operations, then higher Pb concentrations in the sediment would be expected. Another possible explanation is the release of Pb from polluted soils over a long period after the massive pollution. This aspect is currently being investigated. The change in the isotopic ratio of the sample from 45 mm indicates, following the above reasoning, either the end of pre-industrial mining activities or the exhaustion of at least the most mobile fraction of pollutant Pb stored in the catchment area.

The question of who was operating the mines in the Pyrenees in the c. 467 - 1105 AD period remains open. Roman remains exist in this area. No mining is historically or archaeologically documented, although it could well have taken place and so might be the cause of the initial rise of Pb concentration. But the largest Pb peak occurred after Roman times, in a period in which emissions at a continental scale were at a minimum. The fact that pollutant Pb had the same isotopic signature as the Pb deposited from mining during this century in the nearby areas demonstrated that mining on a relatively large scale was taking place in the region in this period.

5. Conclusions

Our data clearly showed an increase of anthropogenic Pb released to the atmosphere starting around 670 BC, in good agreement with the accepted chronologies for Pb pollution at a large scale. A surface peak of Pb concentration appearing in the lake sediments showed a straight relation with the mining activities in the nearby areas. A deeper peak appeared with Pb levels higher than those in the modern one. This peak corresponded to about 658 AD. Coincident isotopic signatures revealed that Pb in both peaks must have the same origin. Mining and smelting at a relative large scale should have then taken place in the surrounding area during post-Roman times.

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