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ORIGINAL PAPER

Tracking past mining activity using trace metals, lead isotopes and compositional data analysis of a sediment core from Longemer Lake, Vosges Mountains, France

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Abstract A 157-cm-long sediment core from Longemer Lake in the Vosges Mountains of France spans the past two millennia and was analyzed for trace metal content and lead isotope composition. Trace metal accumulation rates highlight three main input phases: Roman Times (cal. 100 BC–AD 400), the Middle Ages (cal. AD 1000–1500), and the twentieth century. Atmospheric contamination displays a pattern that is similar to that seen in peat bogs from the region, at least until the eighteenth century. Thereafter, the lake sediment record is more precise than peat records. Some regional mining activity, such as that in archaeologically identified eighteenth-century mining districts, was detected from the lead isotope composition of sediment samples. Compositional data analysis, using six trace metals (silver, arsenic, cadmium, copper, lead and zinc), enabled us to distinguish between background conditions, periods of mining, and of other anthropogenic trace metal emissions, such as the recent use of leaded gasoline.

Keywords Lake · Atmospheric deposition · Smelting · Sediment core · Paleopollution

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Introduction

Human-mediated trace metal (TM) emissions to the atmosphere began several millennia ago, first from mining and smelting operations, and more recently as a result of fuel consumption (coal, leaded gasoline) and industrial or domestic emissions (Nriagu 1996). Such emissions have disrupted biogeochemical cycles, causing ecological impacts on ecosystems at several levels of biological organization (Roodbergen et al. 2008). Reconstruction of past TM emissions requires chronological records that preserve atmospheric inputs. Lake sediments are natural archives that can be used for this purpose, as they record at multiple temporal and spatial scales (Aebischer et al. 2015; Bäckström et al. 2006; Cooke et al. 2007; Renberg et al. 2001, 2002; Walraven et al. 2014). Moreover, they have the potential to provide rapid and continuous reconstructions, unlike historical/archaeological data, which can be sporadic in time, and take longer to acquire, e.g. through documentary research or archaeological excavations.

Large-scale TM deposition is now relatively well documented, at least throughout Europe, for the past two millennia (Meriläinen et al. 2011; Renberg et al. 2002; Thevenon et al. 2011). Other studies have detected more local signals of past mining/smelting activities (Bindler and Rydberg 2016; Bindler et al. 2011; De Vleeschouwer et al. 2014; Kempter and Frenzel 2000; Martínez Cortizas et al. 2013; Mighall et al. 2014; Monna et al. 2004). Lead (Pb) isotopes are often used to track the origin of Pb. Each Pb source, i.e. ore deposit, possesses its own isotopic signature, acquired during its formation, which is generally different from that of the local geological background. It should be noted, however, that TMs recorded in natural archives represent a mixture of several signals that originated from remote sources, as recorded in Greenland ice cores (Boutron et al. 1995) or in Tierra del Fuego (De Vleeschouwer et al. 2014), and regional and local sources (Bindler and Rydberg 2016). Although the Pb isotope approach is considered to be very powerful, it may fail on its own to estimate the respective contribution of each of these sources, in part because (a) their isotopic compositions are, by nature, mostly collinear, and (b) several distinct sources may possess the same isotopic signature. To overcome this difficulty, and especially to extract information concerning local emissions, it is advisable to study several archives scattered throughout the area of interest, but located at different distances from presumed past emission sources. Differences observed between the recorded signals should reflect the influence of local emissions.

Among the most active former mining sites in Europe, the Vosges Mountains are rich in metalliferous ores and have been exploited intensively for Pb, silver (Ag), copper (Cu) and zinc (Zn) over the last millennium (Fluck 2000). Only three TM records have been studied in this area, which covers about 6000 km^2. Two ombrotrophic peat bogs were investigated by Forel et al. (2010) and a minerotrophic marsh was studied by Mariet et al. (2016). The three sites are located close to different known former mining/smelting districts. Although two of them, Rossely and Gazon-du-Faing, have a lot in common, they can sporadically exhibit different histories because of the influence of local inputs. For this study we collected a sediment sequence from Longemer Lake, located in a non-mining valley. It was analyzed for its TM concentrations and Pb isotope composition to infer the regional history of mining/smelting activities. The data obtained were processed using compositional data analysis, an innovative way to identify changes in TM sources. Besides improving the understanding of the local archaeology, these new data offer an opportunity to compare, at small scale, geochemical signals recorded in the two major types of archives used to reconstruct past TM inputs: peat bog/minerotrophic marsh and lake sediments.

Study site

Longemer Lake (N 48°4′25.011″, E 6°56′59.792″, 750 m.a.s.l.) is located in the Vosges Mountains, north-eastern France (Fig. 1). It has a surface area of 76 ha, with a catchment area of 7.8 km^2, and is mainly forested with conifer plantations and mixed hardwood forest. Geologically, the watershed is dominated by gneiss (Fluck et al. 1978; Ménillet and Fluck 1976). Anthropogenic pressure on the lake is low. There is no town in the catchment, only small roads and some tourism infrastructure around the lake. No mining or smelting sites have been identified in the catchment. The lake is about 30 km from the Le Hury site studied by Mariet et al. (2016), 8 km from the Gazon-du-Faing peat bog and 30 km from the Rossely peat bog. The latter bog records were analyzed by Forel et al.

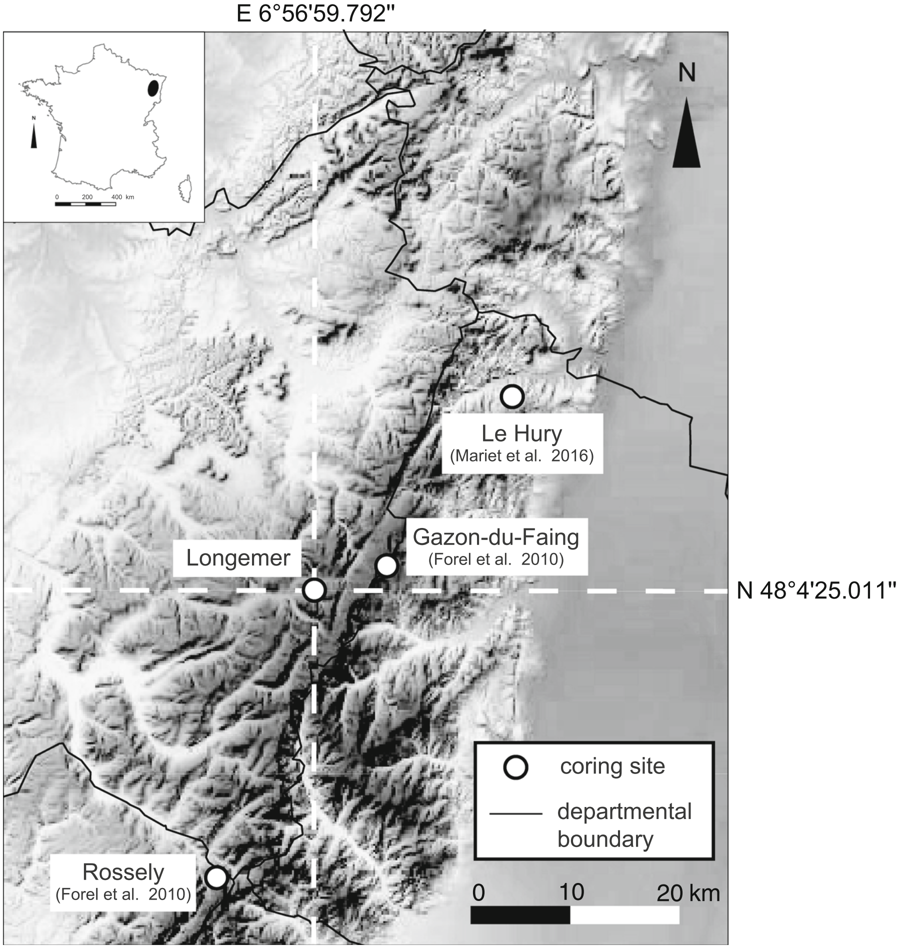

Fig. 1 Elevation map of the Vosges Mountains and site location of Longemer Lake and other sites studied for TMs by Forel et al. (2010) for Rossely and Gazon-du-Faing, and by Mariet et al. (2016) for Le Hury

(2010). The Le Hury site is located in a former Pb–Ag mining district. Gazon-du-Faing is located near past Pb smelting sites and Rossely is situated near former mining districts, in the south of the mountains, i.e. in the mining district of Plancher-les-Mines.

Materials and methods

The core was obtained in summer 2013 near the site of maximum water depth in the lake (30 m), using a 90-mm-diameter UWITEC gravity corer. The core was 157 cm long.

Chronology

Four AMS ^{14}C dates were obtained on terrestrial remains at core depths of 51, 71, 103 and 151.5 cm (Table 1). Radiocarbon dates were calibrated using the IntCal09 ^{14}C calibration curve. For ^{210}Pb dating, the uppermost 19 cm were subsampled evenly and contiguously at intervals of 1 cm. Samples were dried at 60 °C for 72 h. ^{210}Pb, ^{241}Am and ^{137}Cs activities were measured by gamma spectrometry using well-type Germanium detectors in the Modane underground laboratory (LSM/Radionuclides Unit, Chrono-Environment). ^{210}Pb activity was measured after 3 weeks of equilibration in a sealed container. The age-depth relation for the core was determined from excess ^{210}Pb activity, obtained by subtracting ^{226}Ra activity from the measured total ^{210}Pb activity, using

Table 1 Uncalibrated ^{14}C dates and calibrated years BC/AD for the Longemer Lake sediment core

Lab. Code	Depth (cm)	Material	^{14}C uncalibrated years BP	Calibrated years BC/AD (2σ range)
Poz-62620	51	Leaf/terrestrial	460 ± 30	Cal. AD 1413–1465
Poz-56842	71	Leaf/terrestrial	945 ± 30	Cal. AD 1025–1156
Poz-62621	103	Leaf/terrestrial	1670 ± 40	Cal. AD 254–436
Poz-56844	151–152	Leaf/terrestrial	2170 ± 30	360–270 Cal. BC

the constant rate of supply (CRS) model (Appleby and Oldfield 1978). The reliability of the ^{210}Pb-based age-depth model was checked using peaks of ^{137}Cs and ^{241}Am in the record, which are easily identified in lake deposits from the Vosges Mountains. The peaks correspond to the maximum fallout intensity from atmospheric nuclear weapon tests in 1963, and the Chernobyl nuclear accident in 1986 (Kreiser et al. 1992). The age-depth model was then developed from all chronological information by linear interpolation, using the Clam program (Blaauw 2010) for free R (ver 3.2.2) statistical software (R Core Team 2014) (Fig. 2).

Sampling design and physical/chemical characteristics of the core

A total of 42 samples with a thickness of 1 cm were selected every 3 cm, along the 157-cm length of the core. They were freeze-dried to determine water content and prepare material for further analyses. Dry bulk density was determined by weighing dry sediment after freeze-drying a known wet volume of sediment. The linear sedimentation rate was determined from the age-depth model and expressed in cm year^{-1}.

Trace metal analyses

About 250 mg of freeze-dried and ground sediment were digested in *aqua regia* (Yafa and Farmer 2006) (HCl:HNO$_3$, 2.5:1, v/v, Suprapur® grade, Sigma Aldrich), using the DigiPREP graphite block digestion system. Six TMs were chosen because they are enriched in local ores and were targeted by miners (Ag, Cu, Pb and Zn), or because they were emitted into the environment during mining and smelting processes (arsenic [As] and cadmium [Cd]) (Fluck 2000). These TMs were measured on an ICP-MS Thermo X2 Series at the Chrono-Environment laboratory. Certified

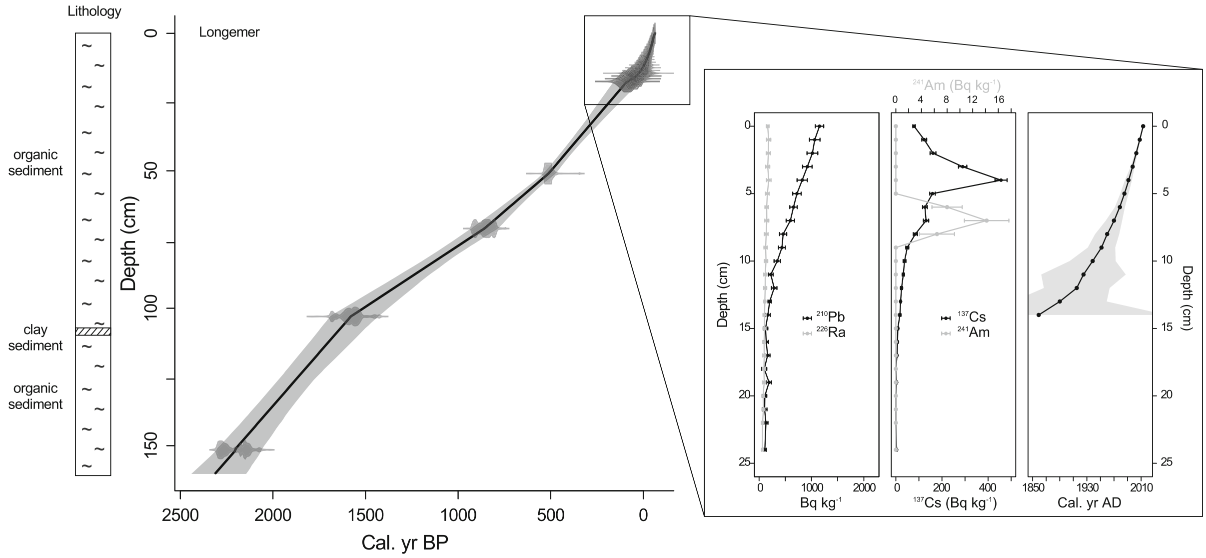

Fig. 2 Lithology and age-depth model for the Longemer Lake sediment core

reference materials (CRM052 Loamy Clay 1) were processed together with study samples. Recovery rates were between 86 and 128%, depending on the TM (Table S1).

Trace metal accumulation rates (ARs) were calculated according to the following equation (Eq. 1).

$$\mathrm{AR} = \mathrm{TM} * \text{dry bulk density} * \text{sedimentation rate} \tag{1}$$

with *AR* in µg cm^{-2} year^{-1}, *TM* is the concentration in µg g^{-1}, the dry bulk density in g dry cm^{-3} wet and the sedimentation rate in cm year^{-1}.

Lead isotope analyses

About 100 mg of each sample were mixed with three acids (HNO_3, HCl and HF) and placed on a hot plate at 120 °C. Once totally digested, Pb was extracted from the matrix using a chromatographic column containing AG1-X8 resin (Cloquet et al. 2006). After being fixed in 0.8 M HBr, Pb was recovered in 6 M HCl (Manhès et al. 1980) and evaporated. After redissolution in 0.3 M HNO_3, isotope analysis was performed using a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (Thermo Scientific Neptune Plus) at the CRPG (Nancy). An international standard solution of SRM 981 mixed with Tl SRM 997 was measured to correct instrumental mass bias. We used both external normalization and the standard-sample bracketing technique with DS TIMS values (Thirlwall 2002), as described earlier (De Muynck et al. 2007; White et al. 2000). In addition, accuracy and long-term reproducibility were ensured using GSD 10 (river sediment) and BCR 482 (lichen) reference materials (Cloquet et al. 2015). Total Pb procedural blanks obtained during the course of the study were stable at around 300 pg.

Compositional data analysis

Compositional data analysis is a statistical method adapted to closed data, which usually sum up to a constant (which is the case for almost all geochemical data). It compensates for problems related to the bias of the covariance structure of compositional data, which casts doubt, without appropriate transformation, on any multivariate statistics based on the correlation matrix (Filzmoser et al. 2009).

Here, the elemental composition of a sample is defined by a vector of D trace metal concentrations ($\boldsymbol{x} = [x_1, x_2, \ldots, x_D]$). First, this compositional vector is transformed using centered log-ratio (*clr*) transformation (Eq. 2) to circumvent problems related to the closed nature of compositional data (see Aitchison 1982, 1986, for theoretical development and Meyer et al. 2015; Pasquet et al. 2016, for environmental application).

$$clr(\boldsymbol{x}) = \left[\ln\frac{x_1}{gm(\boldsymbol{x})}, \ln\frac{x_2}{gm(\boldsymbol{x})}, \ldots, \ln\frac{x_D}{gm(\boldsymbol{x})}\right] \tag{2}$$

with x_1, x_2, …, x_D corresponding to the concentrations of the different TMs measured in the sediment sample, while $gm(\boldsymbol{x}) = (x_1, x_2, \ldots, x_D)^{1/D}$ represents the geometric mean of the D parts of the compositional vector.

The transformed data were processed using the covariance biplot (Aitchison and Greenacre 2002). Some properties of the compositional biplot must be mentioned to facilitate interpretation. First, unlike for traditional biplots (Gabriel 1971), the rays formed by individual components cannot be interpreted. Only links between “arrowheads” of variables are meaningful; they approximate the standard deviations of the log-ratios of these variables, whereas the angle cosines between links estimate correlations between two log-ratios (van den Boogart and Tolosana-Delgado 2013). For example, when two links are orthogonal, there is no correlation between the two log-ratios, whereas when components lie on the same line, their log-ratios are either strongly positively (or negatively) correlated. Note that the importance of absolute concentration values is lost during this statistical analysis. Only ratios between components make sense, and individual components, taken separately, cannot be interpreted, like for the classical Gabriel’s biplot.

Results

Chronology and core characteristics

The core spans more than the past two millennia, and no ^{14}C date reversals were observed (Fig. 2; Belle et al. 2017). The standard deviation of the age-depth model varied between 140 and 80 years from 300 BC to AD 670, between 80 and 10 years from AD 670 to

AD 1980 and from 10 to 1 years from AD 1980 to present. Although at the whole-core scale the sedimentation rate was relatively constant, it varied at times, from 0.044 cm year^{-1} at a depth of 1 m, to 0.265 cm year^{-1} at the top (Table S2). As expected, because of sediment compaction, dry bulk density (g dry cm^{-3} wet) increased from the top (0.075 g cm^{-3}) to the bottom of the core (0.196 g cm^{-3}).

Trace metal concentrations and accumulation rates over the past two millennia

All trace metal concentrations displayed the same general pattern. They increased dramatically from the core base to the top by a factor of ten for Pb (Fig. 3a, Table S2), four for As (Fig. 3b), eight for Cd and Zn (Fig. 3c, d), and two for Cu and Ag (Fig. 3e, f). The main increase occurred in recent times, approximately from the nineteenth century onwards (Fig. 3, Table S2). Expressed as ARs, this increase is even greater, given the higher mass sedimentation rate close to the core top (Figs. 2, 3).

Lead isotopic compositions

The ^{206}Pb/^{207}Pb ratios vary from 1.23 at the bottom of the core, up to 1.16 at the surface (Fig. 3a). Besides this overall decrease, the ^{206}Pb/^{207}Pb ratios exhibit a noticeable decline in Roman Times (to 1.19; Fig. 3a). From about AD 1000 to the surface, the ^{206}Pb/^{207}Pb ratios continue to decrease irregularly, never returning to the value of 1.23 found at the base of the core. Plotted in a ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb diagram, the core samples roughly define a line (Fig. 4a). Samples older than AD 1000, except those corresponding to Roman Times, are the most radiogenic, whereas recent samples, deposited since about AD 1950, are the least radiogenic (Fig. 4a). The Pb isotope composition of the three major local ores, named (Marcoux 1987) (a) "A", corresponding to high-temperature deposits, (b) "B", consisting of F/Ba and Ag/Pb veins and presenting the most radiogenic isotopic compositions, and (c) the Lusse type, which is intermediate between the two previous ores, are all shown in Fig. 4a, b for comparative purposes (Table 2).

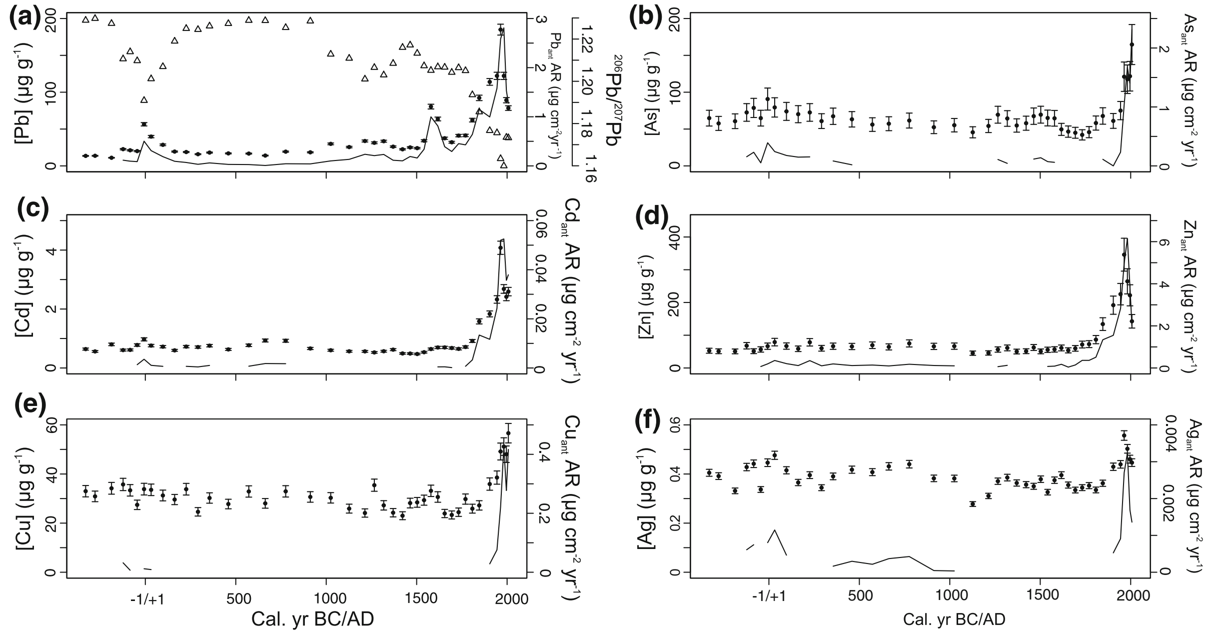

Fig. 3 **a** Pb concentrations (solid circles, µg g^{-1}), ^{206}Pb/^{207}Pb (empty triangle) and anthropogenic Pb accumulation rates (Pb$_{ant}$ AR, solid line, µg cm^{-2} year^{-1}). Concentrations (solid circles, µg g^{-1}) and anthropogenic ARs (TM$_{ant}$, solid lines, µg cm^{-2} year^{-1}) of **b** As, **c** Cd, **d** Zn, **e** Cu and **f** Ag. Note that when the line representing anthropogenic AR is discontinuous, it means the absence of anthropogenic input

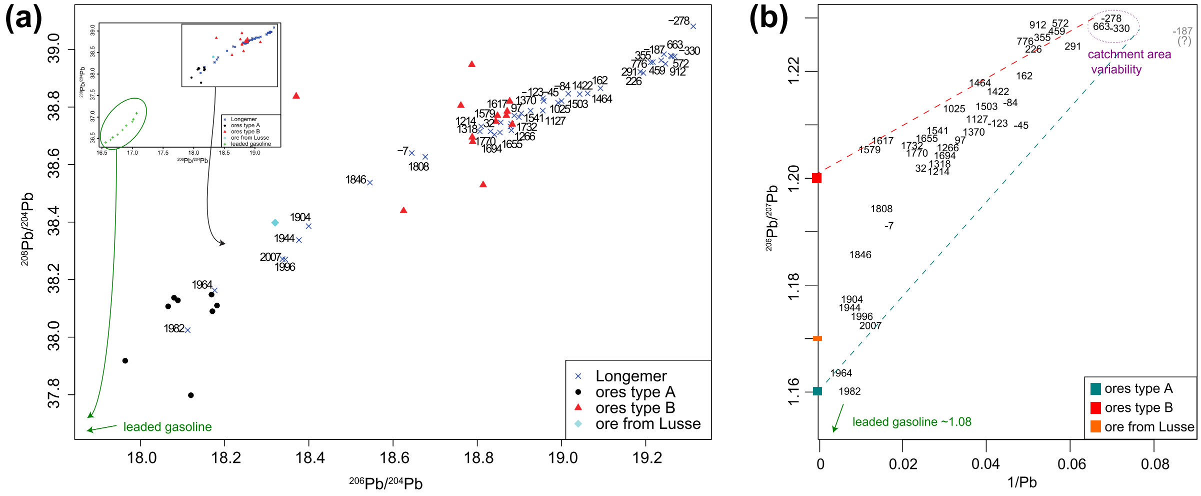

Fig. 4 **a** ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb of samples from the Longemer Lake sediment core and potential sources of type A ores, type B ores, ore from Lusse and leaded gasoline (Marcoux 1987; Monna et al. 1997). Numbers represent the calibrated years BC/AD of samples along the core. **b** ^{206}Pb/^{207}Pb versus 1/Pb of samples from the Longemer Lake sediment core, with potential sources for mining activities as type A ores, type B ores and ore from Lusse (Marcoux 1987). Numbers represent the calibrated years BC/AD of the samples along the core. Dashed lines correspond to the potential mixing of sources

Table 2 Lead isotope ratios of potential sources in the Vosges Mountains. Lead isotope ratios of the three types of ores are taken from Marcoux (1987), those of leaded gasoline, urban incinerator ashes and airborne particulate matter are taken from Monna et al. (1997)

References	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{208}Pb/^{206}Pb	^{206}Pb/^{207}Pb
Ores type A (n = 8)	18.1051 ± 0.0726	15.5716 ± 0.0206	38.0545 ± 0.1268	2.1019 ± 0.0088	1.1625 ± 0.0034
Ores type B (n = 13)	18.7789 ± 0.1411	15.6494 ± 0.0333	38.7358 ± 0.1315	2.0628 ± 0.0167	1.200 ± 0.0108
Ore from Lusse (n = 1)	18.32	15.64	38.398	2.096	1.171
Leaded gasoline (n = 9)	16.8283 ± 0.1792	15.526 ± 0.0325	36.7144 ± 0.2337	2.1817 ± 0.0097	1.0839 ± 0.0096
Ashes from urban incinerator of Sète (n = 4)	17.9868 ± 0.0684	15.6470 ± 0.0435	38.0575 ± 0.1325	2.1158 ± 0.0070	1.1495 ± 0.0050
Airborne particulate matter of Strasbourg (n = 2)	17.5885 ± 0.0318	15.5240 ± 0.0481	37.3650 ± 0.0778	2.1243 ± 0.0010	1.1331 ± 0.0016

"n" represents the number of samples included in the calculation of Pb isotope ratios (mean ± SD)

Compositional data analysis

The first two components of the biplot explained 91% of the total variance (Fig. 5), a fairly high value for six variables. Silver, Cu, and As, on the one hand, and Cd and Zn, on the other hand, plot relatively close to each other (i.e. their links are short), indicating relatively constant log-ratios among the variables that compose these groups. Lead lies apart. The largest links are observed between Pb and Ag, Cu and As. They illustrate the largest relative variations across the samples. The biplot also highlights clear compositional changes over time (in terms of elemental ratios), as samples are mostly distributed chronologically on the diagram. The oldest samples, i.e. from 330 BC to the end of the first millennium AD, plot apart, in the lower left part of the diagram, to form a group named I (Fig. 5). Those from the period up to the beginning of the nineteenth century (group II) correspond to the upper-middle part of the biplot, whereas the most recent samples plot in the lower right (group III; Fig. 5). Note that only two samples, 7 BC and AD 32,

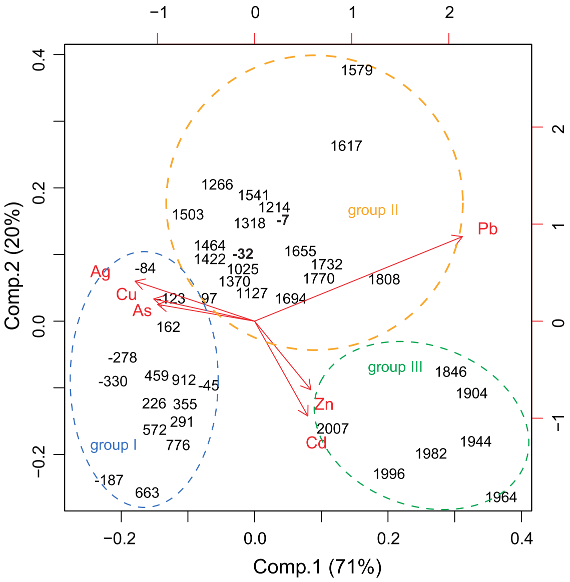

Fig. 5 Covariance biplot of compositional data analysis. Numbers represent the calibrated years BC/AD of the samples along the core. The three groups of dates (I, II, III) correspond to three time periods with different inter-element compositions

do not fit this general pattern, as they plot in group II (Fig. 5).

Discussion

Background definition

As mentioned above, samples older than Roman Times have the highest $^{206}Pb/^{207}Pb$ ratios ($\sim$ 1.23), and are separated from the rest of the core samples in the biplot diagram (group I) because of their specific chemical composition. It is unlikely that these samples represent the true background, as other studies undertaken in natural archives around the Vosges Mountains indicate that atmospheric deposition of metals from mining and metallurgical activities started as early as the Bronze Age since 2000 BC (De Vleeschouwer et al. 2010; Monna et al. 2004). Nonetheless, several factors support use of these three samples to estimate the local background, at least as a first approximation. No mining activity in the Vosges Mountains has been recognized before Antiquity, i.e. prior to about AD 900. Even if such activity took place around the region, it was not intense enough to affect the Vosgian lakes. Moreover, $^{206}Pb/^{207}Pb$ ratios around 1.23 are among the most radiogenic values ever measured in the area, and the Pb from local ores is all less radiogenic. It is also worth noting that sample concentrations are obtained from strong *aqua regia* digestion. Only naturally derived metals are extracted, in part because metals incorporated in the lattice network of minerals are largely unaffected. All anthropogenic (acid soluble) metals should be removed by the strong *aqua regia* leaching, because they remain adsorbed to the surface of minerals. Considering the low concentrations of all metals in the three deepest samples, together with the key arguments stated above, it is reasonable to use them as estimates for natural inputs.

Anthropogenic contribution

The anthropogenic contribution to the total concentration can thus be calculated by subtracting the background contribution, which is assumed to have been constant through time. If two components are involved, a natural and an anthropogenic one, the mixing model $^{206}Pb/^{207}Pb = f(Pb)$ is a hyperbolic curve (Faure 1986), which can be transformed into a straight line using a ($^{206}Pb/^{207}Pb$) versus 1/Pb plot (Monna et al. 2000b). In such a diagram, the intercept at the Y-axis of a line linking the background to any of the contaminated samples, i.e. those containing Pb from a source other than the background one, represents the isotopic composition of this contamination source. Figure 4b depicts our samples, in which the background plots at about 1/Pb = $\sim$ 0.06–0.07, and $^{206}Pb/^{207}Pb$ = $\sim$ 1.23. The higher the Pb concentration (i.e. the lower the 1/Pb), the better the estimation of the isotopic value of the anthropogenic component. If the less contaminated samples are eliminated, because they are less constrained, the isotopic composition of the anthropogenic component alone varied between approximately 1.16 and 1.20 (Fig. 4b).

A chronological history of regional mining activities

Accumulation rates of anthropogenic Pb in Longemer (0–2.8 µg cm^{-2} year^{-1}; Fig. 3a), are in the same range as anthropogenic Pb fluxes calculated for Gazon-du-Faing, which varied from 0 to 1.2 µg cm^{-2} year^{-1}, and those of Rossely, which ranged from 0 to 4 µg cm^{-2} year^{-1} (Fig. 6). The three

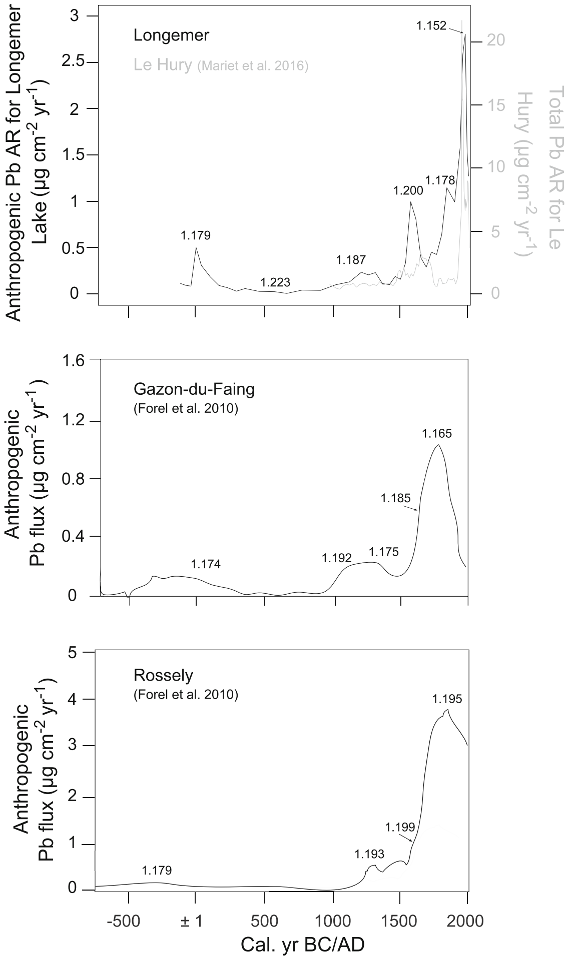

Fig. 6 Anthropogenic Pb accumulation rate (AR, µg cm^{-2} - year^{-1}) in the Longemer Lake sediment core, total Pb AR for Le Hury (grey line, Mariet et al. 2016), and anthropogenic Pb fluxes for Gazon-du-Faing and Rossely (Forel et al. 2010) cores. Anthropogenic ^{206}Pb/^{207}Pb ratios are reported on the graphs for the Longemer, Gazon-du-Faing and Rossely cores

sequences are also similar in terms of shape, despite the fact that they sporadically exhibit significant differences, which are discussed below.

Lead concentrations in the deepest samples (cal. 330–187 BC) of the Longemer sequence ranged between 11 and 14 µg g^{-1}. Such values are comparable to those generally found in Europe for undisturbed or only slightly human-impacted lakes (Renberg et al. 1994; Thevenon et al. 2011), or the minerotrophic marsh of Le Hury (Mariet et al. 2016). Lead concentrations in the ombrotrophic peat bogs of Gazon-du-Faing and Rossely (Forel et al. 2010) are much lower (< 1 µg g^{-1}). In addition, the bulk ^{206}Pb/^{207}Pb ratios are higher in Longemer Lake (^{206}Pb/^{207}Pb = ∼ 1.23; Fig. 3a) than in the two peat bogs from Forel et al. (2010) (^{206}Pb/^{207}Pb = ∼ 1.17). Such discrepancies can be explained easily by incorporation of Pb of a different nature. Peat is fed almost exclusively by atmospheric dust inputs, and does not integrate minerals from runoff-derived material in the local catchment area, as is the case for lakes (Brännvall et al. 1997).

Since the beginning of our era, i.e. over the past two millennia, the shift in anthropogenic Pb concentrations suggests the introduction of human-derived Pb into the sediment sequence. This can also be observed for Cd, As, and to a lesser extent for Zn (Fig. 3). In the covariance biplot, these samples move away from the background samples, in part as a consequence of the influence of the increase in Pb concentration (Fig. 5). Such an anthropogenic input is also clearly confirmed by the concomitant decrease in Pb isotope composition, a measure known to be much more sensitive than Pb concentrations to identify low anthropogenic inputs. In Fig. 6, the ^{206}Pb/^{207}Pb ratio of the anthropogenic contribution at that time can be calculated as 1.179, using the equation of Monna et al. (2000a). An increase in Pb was also observed in La Gruère peat in Switzerland (Shotyk et al. 1997, 2001), but in Gazon-du-Faing and Rossely, no clear shift in Pb isotopic composition was observed. This may be a consequence of the isotopic similarity between background in the Gazon-du-Faing and Rossely sequences (^{206}Pb/^{207}Pb = ∼ 1.17–1.18), and that of the pollutant (^{206}Pb/^{207}Pb = ∼ 1.174–1.175 and 1.178–1.179). Comparable Pb isotope values of the anthropogenic contribution alone were also calculated for the La Gruère sequence (^{206}Pb/^{207}Pb = ∼ 1.176–1.177). Such an intensification of anthropogenic atmospheric inputs has been reported at the continental scale, even at high latitudes such as Greenland (Hong et al. 1994; Rosman et al. 1997) and Sweden (Brännvall et al. 1999; Renberg et al. 2001) during Antiquity. These signals are so ubiquitous that Renberg et al. (2001) proposed using them as a chronological marker in sediments. Anthropogenic inputs during Antiquity are supposed to have originated, after long-range transport, from metals exploited in remote areas, such as the Rio Tinto site in Spain (Rosman et al. 1997). The metals measured in Longemer Lake sediments undoubtedly derived from this common European origin, especially as there is no archaeological evidence of mining in the Vosges until the tenth century (Fluck 2000). After the fall of the Roman Empire (AD 1453), the decline in metal production throughout Europe is recorded in our sediment sequence, as multiple metals and Pb isotopes trended toward background values, but never reached them (Fig. 5, group I).

After AD 1000, ^{206}Pb/^{207}Pb ratios in the Longemer Lake record decreased. Lead ARs increased simultaneously. This is less clear for other TMs, although a change in elemental ratios can be observed in Fig. 5. This finding is in good agreement with knowledge of the local history, as the oldest artifacts related to local mining date from the ninth–tenth centuries. A first Pb peak around AD 1250–1300 is recorded in Longemer Lake, similar to other Vosgian sequences (Fig. 6). Its magnitude, in terms of AR, is similar to that of the previously discussed ancient peak.

From AD 1300 to 1500, the return of the ^{206}Pb/^{207}Pb ratio towards background values is consistent with a decrease in mining activities at the regional scale, related to a demographic decline following the Black Plague and several episodes of famine. These events caused the death of almost 50% of the population during the fourteenth–fifteenth centuries (Fluck 2000). Such a Pb AR decline is also registered in the Gazon-du-Faing and Rossely peat bogs (Forel et al. 2010), but not in the Le Hury core (Mariet et al. 2016), since local mining persisted in that particular valley (Fig. 6).

Two samples, dated to AD 1579 and 1617, stand out as distinct in the biplot diagram, partly because of their high Pb concentrations (Figs. 3a, 5). Both samples are contemporaneous with the discovery of new profitable mines, together with the use of the Saigerprozess, which became widespread during the sixteenth century in the Vosges Mountains. The technique improves Ag extraction by adding massive amounts of Pb to copper, as the latter contains Ag. Regional Pb and Ag mining is documented all over the Vosges Mountains at that time, and registered in the former mining district of Sainte-Marie-aux-Mines (Fluck 2000; Mariet et al. 2016). The isotope composition of anthropogenic Pb in Longemer is close to that of type "B" ores (Fig. 4b) and is similar to the anthropogenic signature in Rossely (^{206}Pb/^{207}Pb = $\sim$ 1.200), but not to that for Gazon-du-Faing (^{206}Pb/^{207}Pb = $\sim$ 1.18; Fig. 6), despite the fact that Gazon-du-Faing and Longemer Lake are geographically close (Fig. 1). Mining was present at a regional scale, with the more intensive period of historically known mining in the Vosges Mountains (Fluck 2000). Discrepancies between sediment records are probably attributable to: (a) differences between surfaces onto which atmospherically derived metals fall, (b) distance from the source(s), or (c) the specific nature of the archive (Farmer et al. 1997). These factors are not mutually exclusive. Moreover, Pb content and isotopic composition of natural background and emitted particles can vary a lot within a region, related to aspects of the catchment area, as well as the geologic background or anthropogenic activities around the site, as shown in Scotland by Eades et al. (2002). These natural variations could lead to different values being registered over the same period in relatively close archives, so it is advisable to study multiple sites to obtain a realistic picture of atmospheric contamination at the regional scale. Different post-depositional mechanisms could also drive changes in the TM signal in sediment and peat sequences (Outridge et al. 2011). These include chemical diagenesis, a change in redox state, which alters TM mobility, and erosional processes in the catchment (Brännvall et al. 1997; Liu et al. 2012; Outridge et al. 2011). This intense period of activity (sixteenth–seventeenth centuries) was followed by a rapid decrease in anthropogenic ARs until the eighteenth century. The variations in anthropogenic Pb ARs and Pb isotopic compositions recorded in Longemer Lake confirm the historically known time of instability for mining (Fluck 2000), which was, however, not recorded in the Gazon-du-Faing and Rossely sequences (Forel et al. 2010). Several hypotheses have been invoked to explain the poor accuracy of the peat records: (a) sampling resolution of peat sequences was too low, (b) proximity of mining activities can be an important factor, and even low inputs, which are negligible at the regional scale, can have a considerable impact on archives in the immediate vicinity of mining (Mariet et al. 2016), and (c) the nature of the archive. Peat sequences may be less efficient for preserving high-frequency changes than undisturbed lake sediments (Farmer et al. 1997), because the former develop from living plants, which create a micro-topography that may lead to artifacts in the record (Outridge et al. 2011). Some peats possess roots that penetrate deep into the peat sequence, and can remobilize metals by biological recycling.

Changes in plant species could also affect TM mobility (Liu et al. 2012; Outridge et al. 2011). Peat sequences, however, present some advantages over lake sediments in that the former are easily dated by ^{14}C and their low mineral matter content enables registering a high-quality signal under conditions of low contamination (Brännvall et al. 1997). Differences between lake sediment and peat sequences may lead to differences in the recorded contaminant signal, though there are several examples of remarkable similarities between the signals recorded in the two types of archives (e.g. Brännvall et al. 1997; Farmer et al. 2015), and the present study, except for the eighteenth century.

Since the nineteenth century, all TMs increased sharply because of persistent local mining, but above all, because of massive TM emissions, observed at the continental scale since the onset of the Industrial Revolution. A change in elemental composition is also recorded in Longemer Lake during that time, confirming changes in TM sources. Later, during the second half of the twentieth century, the impact of leaded gasoline is clear, expressed by the fall of ^{206}Pb/^{207}Pb values, which stands as a proxy for the introduction of exogenous lead into the sequence. Such Pb contamination is well documented at the global scale (Brännvall et al. 1997; Moor et al. 1996; Renberg et al. 2002). The decrease in Pb concentration since the 1980s, associated with a return to more radiogenic Pb isotopic ratios, is explained by the progressive phasing out, and then the complete ban on leaded gasoline use in Western Europe. Lahd Geagea et al. (2008) analyzed modern bark, lichen and moss samples for Pb isotope composition, and proposed a baseline, i.e. natural atmospheric Pb isotope value for the Vosges Mountains, of ^{206}Pb/^{207}Pb $\sim$ 1.158–1.167. Such values are similar to Pb isotope ratios of the contamination source found in Longemer Lake in surface and sub-surface bulk samples (Fig. 4b). Indeed, the isotopic composition of the pollutant for the sample dated to AD 2007 is ^{206}Pb/^{207}Pb $\sim$ 1.165 (Fig. 4b), highlighting homogenous regional contamination during the last few decades.

Conclusions

The sediment sequence from Longemer Lake recorded several phases of metal contamination during the last two millennia. As expected, TM inputs observed during Antiquity all across Europe, up to high latitudes, are also recorded in Longemer Lake. Unlike other European sites with local mining and metallurgical activities, such as in Rio Tinto, there is no geochemical indication of early mining. This is in good agreement with the lack of archaeological evidence for early mining in the Vosges Mountains. Similarly, globally observed contamination stemming from the Industrial Revolution, and recent, massive inputs of Pb from the use of leaded gasoline, are identified in the Longemer sequence. At a regional scale, mining only seems to have started in the ninth–tenth centuries. It was followed by a decrease in mining during the fourteenth–fifteenth centuries, which is documented in all the known sequences from the Vosges Mountains. The change in the smelting process that resulted from use of the Saigerprozess during the seventeenth century, and the following period of mining instability in the eighteenth century, are recorded with high precision in Longemer Lake. The sediment core from Longemer Lake, for the first time in the Vosges Mountains, shed light on short-term variations in contamination. Such fluctuations were not detected in peat sequences. Analysis of TM concentrations by compositional data analysis facilitates the detection of TM source changes in an integrated and innovative way. The position of each individual sample in the compositional biplot illustrates its elemental ratios, simplifying comparisons between samples. Combining this information with Pb isotope composition, which is highly sensitive to low Pb contamination, could be very useful for developing more precise reconstructions of atmospheric inputs to lake sediment or peat sequences.

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