Identification of heavy metal contamination in lake sediments using lead isotopes: the case of Saint-Point and Grand Maclu lakes (France)

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Abstract

The production of drinking water enters a crucial phase as soon as the sources of contamination multiply and extractions increase. Numerous studies have looked at limnic reserves with a strong heritage character, often used to meet the drinking water needs of communities. They highlight the state of degradation of the water bodies and the need to restore them urgently and enhance the water productivity. Most of them focused on the trophic status of the water bodies, the excess of nutrients and chemical inputs of agricultural origin, whose origin remains local. Analyses of water quality have shown relatively high levels of heavy metals (40 - 100 µg/l), casting doubt on the actions taken to collect waste on the scale of local catchment areas. Contents in the sediments fluctuate between 50-100 µg/g, of which a significant proportion is diluted in the interstitial (pore) water. All Alpine and Jura water bodies show traces of metals since the end of the 19th century. The concentrations recorded in the waters of the Jura lakes are of the order of 3-10 µg/g at the surface and can reach 20-35 µg/g at depth, particularly during the stratification period, making the hypolimnion highly anoxic (oxygen content < 2-5%) and a pH slightly below 7. Almost all the water bodies in the Alps and the Jura are directly affected by the consequences of these malfunctions, in particular, those caused by industry (foundries, coal mining), releasing metal emissions, thus affecting the quality of the water and sediments of these fragile reserves. The levels of certain heavy metals recorded in two lakes in the French Jura (Maclu and Saint-Point) confirm the findings of numerous studies on other lakes, highlighting the remote origin of emission sources outside the catchment areas.

Keywords: Eutrophication; Water Productivity, Heavy Metals; Jura; Lakes; Nutrient; Sediment; Watershed

INTRODUCTION

Lakes are complex and fragile ecosystems. Many of these water bodies are constantly threatened by different types of pollutants and harmful elements (Dvinskikh and Larchenko, 2021). Numerous studies focused on limnic entities, which often possess a significant cultural value and are used to meet the potable water needs (Isabelle Larocque-Tobler, 2017). Many of these studies highlight several forms of degradation in these water bodies and raise the need for urgent restoration. In order to reduce the often threatening human-induced pressure on these ecosystems, concrete measures have been put in place for decades, with most aiming to reduce local pressures (Schallenberg and Schallenberg, 2017). While many approaches have been practical, challenges arise when waterbodies of distant origin and falling under different jurisdictions are the source of the problem. It is due to the fact that these are not under the control of

local decision-makers but are subjected to international laws that are, in most cases, difficult to circumvent. Water bodies restoration, especially those of importance for local communities and countries, has become a priority under all water body management or preservation policies. Most of the proposed solutions aim to respond to eutrophication problems caused by the abundance or even excess of nutrient inputs (N, P) (Søndergaard, 2007; William, *et al*., 2018; Tao *et al*., 2020). Excess N and P inputs lead to a progressive entry of water masses, especially those in the hypolimnion, into a phase of anoxia through the drastic reduction of oxygen levels during periods of stratification.

In response to this situation, undertaken measures aim to reduce anthropogenic pressure on the catchment areas (wastewater collection, reduction of livestock farming and collection of nitrogen and phosphorus discharges, controlled agricultural practices, etc.). As a result, many water bodies show a clear improvement in trophic levels. However, in terms of water quality, the concentration of some metals remains worrying as they continue to increase despite the measures taken (Bao *et al*., 2020). Several questions regarding the origin of these inputs continue to be raised since they do not correspond to local discharges, which are often removed in their movement in the watershed.

Numerous studies carried out on the large Alpine lakes (France, Switzerland, Germany, etc.) confirm after sediment analysis that for almost a century (end of the 19th and until the beginning of the 20th century), heavy metal content has significantly increased (Shotyk *et al*., 2001.2003; Arnaud *et al*., 2003, Arnaud, 2003; Aboud and Nandini, 2006). This observation is not limited to southern European countries and extends to northern Europe and the American continent (Punning *et al*., 1997). Thus, Renberg *et al*. (1994); Shotyk *et al*. (1998); Arnaud (2003) studies on lakes confirms this trend and gives a pattern almost similar to what

was found in France.

The waters of the Jura lakes (France), well-known for their quality and purity, are an economical and heritage asset of exceptional regional importance. Their preservation and protection are at the centre of debates at different levels of the regional decision-making hierarchy. The related 2008 and 2009 decrees are the very translation of the desire to preserve these fragile reserves. Faced with water quality challenges, the source identification of various chemical elements that can affect the quality of these reserves became a necessity. Geochemical investigations carried out on samples of sedimentary columns, on the water columns and interstitial water sampled from 9 lakes reveal a double trend marked by an inflexion at the level of three the curves that correspond to three metals (Cr, Zn, Cu) dating back from the end of the 19th century (1890), and that are responsible for an increase of chemical inputs in these lakes.

These findings highlight the rise in the concentration of these elements due to the booming of heavy metal related industry throughout the western world back in the late 1890s. The sources were pinpointed through isotope analysis, where the isotopic ratios of lead ($206Pb/207Pb$), with values 1.15-1.16 at the inflow peak, proved the involvement of a global industrial dynamic (addition of lead into petrol during the 1920s in the USA and 1930s in Europe). The local influence of these metallic inputs was quickly ruled out following studies of wastewater and other domestic/industrial discharges performed in the 1970s.

Nevertheless, the decrease of oxygen levels and the entry of the hypolimnion into reduction redox phase as a result of an impetus of consequent organic contributions linked to the reforestation activities of the 1970s that were carried out by the RTM (Restoration of Mountain Land) services, makes these lakes heavy metal sources rather than sinks. The heavy metal content of the water increases to

values of a few dozen ppm at the base of the hypolimnion during the stratification period (May – October). The chemical profiles of the interstitial waters of the sedimentary columns show significantly high levels in the first thirty centimetres, in manners similar to the geochemical profiles carried of the sediments. A slight difference at the surface (decrease of heavy metal content) is observed due to exchanges with the open water mass.

The aim of this research is Identificating the heavy metal contamination in lake sediments using lead isotopes. This has been performed on Saint-Point and Grand Maclu lakes, France.

STUDY AREA

The Grand Maclu (46°37'52" N; 5°54'56" E) and Saint-Point (46°48'55" N; 6°18'50" E) lakes are located 50 km apart, at about an elevation of 800 a.s.l. in the Jura mountains – France (Figure 1). Both lakes occupy elongated N40-45° depressions of glacial origin, formed from a single basin for the former and two basins for the latter. Maximum depths and surface areas are 25 m and 1.02 km² for Grand Maclu, and 38 m and 5.2 km² for Saint-Point. The Grand Maclu is located at the head of the catchment basin, draining a small surface area of 1.13 km². In comparison, the Saint-Point lake is fed by the Doubs River, which drains a much larger catchment of 7710 km².

Both watersheds possess almost the same geological features, marked by a predominance of limestones and muddy limestones, with occasional sandstone strata, essentially of Jurassic and Cretaceous age. These formations may be locally covered by molassic sediments or more recent morainic layers. The high permeability of heavily karstified limestones allows a through-flow towards the lakes. Several springs punctuate the zone of contact between the lakes and their basins. Water renewal times are short, less than 12 months. The regional climate is of the continental type under a significant oceanic influence, with west-southwest prevailing winds. Precipitation occurs as rainfall during the stormy spring and autumn and mainly as snow during winter. In this region, the average precipitations vary between 2,000 and 2,200 mm per year.
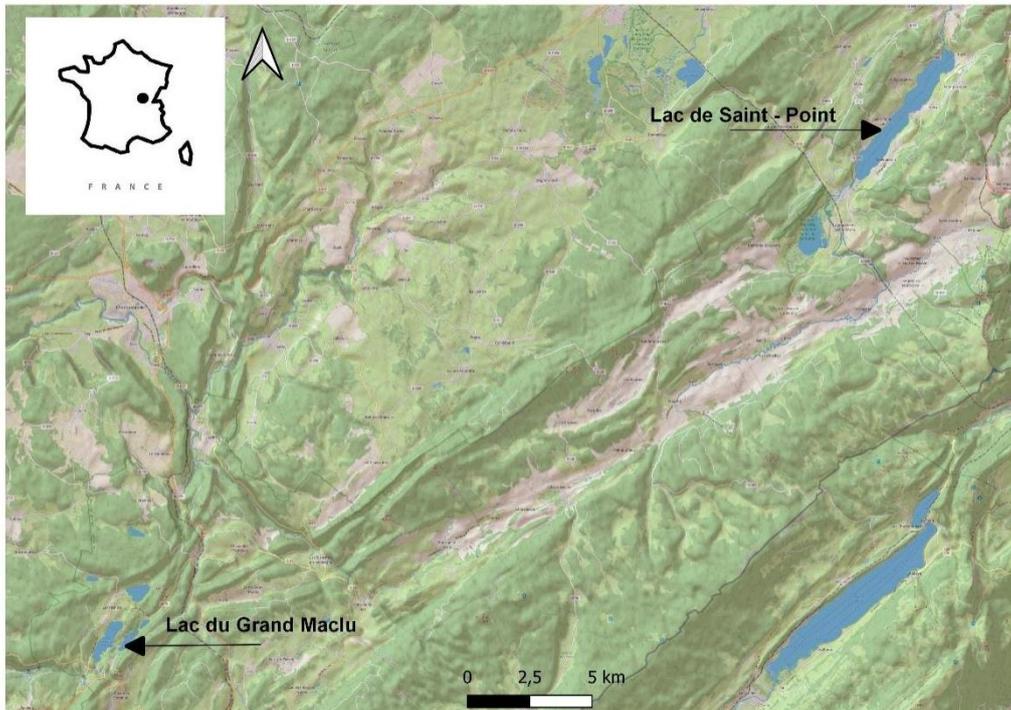

Fig. 1. Site study localization

MATERIALS AND METHODS

A bathymetric map was elaborated with the help of a Syqwest echo sounder, providing data on both water and sediment depth. Sediment coring was carried out at the most profound places characterized by gentle slopes and little-disturbed deposits, using two-meter Plexiglas tubes equipped with a double hermetic corking. At the laboratory, the subsampling was performed at an interval of 1 cm for the uppermost 20 cm, 2 cm for 20-40 cm depth, and 3 cm from 40 cm depth to the base. Half of each sample was dried at 110°C for 24h and at 550°C for 6h to determine water (WC%) and organic matter (OM%) contents, respectively. Dry bulk density was estimated by assuming a density of 1 and 2.6 for organic (OM) and inorganic material (MM), respectively. The remaining samples were freeze-dried and sieved at 64 μm. All geochemical analyses were performed on this finest fraction. Fusion of 200 mg of sediment was operated using 600 mg of lithium metaborate in crucibles (automatic tunnel oven) after the powder was ignited in oxides at 950°C for 2h. It was followed by dissolution in nitric acid 1N. ICP-MS and ICP-OES measured concentrations at the central CNRS laboratory, CRPG, Nancy. The sum of oxides appeared to be between 99% and 101%. The quality control process was ensured by running geochemical standards and appropriate environmental samples. Quadrupole-based ICP-MS analyzed lead isotopic compositions (206Pb, 207Pb, and 208Pb) of the Grand Maclu sediments according to the method described by Krachler *et al.* (2005). For the Saint-Point samples, lead isotopic compositions were made at the CRPG, Nancy, using MC-ICP-MS (Monna *et al.*, 2000.2000a.200b).

Dating was based on the 210Pb and 137Cs methods. Radiochemical analyses were performed in the Liverpool University Environmental Radioactivity Laboratory (UK). Dried sediment samples were analyzed for 210Pb, 226Ra, 137Cs and 241Am by X-ray spectrometry using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby *et al*., 1986). 226Ra was obtained *via* γ-rays emitted by its daughter radionuclide 214Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. Self-absorption and efficiency corrections were made following Appleby *et al.* (1992). Excess Pb (210Pbxs) was obtained by subtracting the total 210Pb, the supported activity (210Pbinsitu assumed to be equal to 226Ra). Age–mass depth models were built using a constant rate of 210Pb supply (Appleby and Oldfield, 1978), allowing mass accumulation rates along the sequences to be calculated (expressed in g cm-2 yr-1). Elemental fluxes were then computed using concentration measurements.

The objective of this paper is to highlight that, despite the concrete actions carried out on many mountain lakes to preserve them from potential pollution, sediments, which for a long time were considered sinks, have become sources of heavy metal emissions stored for nearly 1.5 centuries. These exchanges are primarily due to the profound modification of the limnic systems' state during stratification periods associated with high levels of organic matter in the sediments, arising from the closure of the landscape and the progression of tree vegetation.

RESULTS AND DISCUSSION

Both sequences had about 70 cm in length. They are composed of lacustrine chalk, more or less whitish, depending on the organic matter content and, probably, on the amount and the nature of clay minerals. The Saint-Point core presents a homogeneous clear greyish sequence of about 60 cm depth, which turns into white below. The Grand Maclu core is similar, except that the 5-7 first centimetres consist of dark reduced material, whereas the below 60 cm depth is dark grey. Both cores exhibit expected water content (w/w)

profiles governed by compaction: high values in the uppermost horizon of 80% and 90%, decreasing up to 21 cm and 17 cm, and steady values of 60% and 80% up to the base, for the Saint-Point and Grand Maclu sequences, respectively (Figure 2). In the following figure, the depth scale is expressed in terms of cumulative mass depth (g cm-2) as described in Sugai et al. (1994) to eliminate these porosity variations.

Geochemical and radiochemical results for Saint-Point

OM (Organic Matter) content is about 5-9 % all along the sequence, except in the 5 g cm-2 topmost layers, where it slightly increases. The CaO content varies between 35% and 45% (equivalent to $CaCO_3$ contents between 63% and 83%). It is inversely correlated to TiO_2 (Figure 2). Lithophilic elements (Ti, and Th, Zr, Al, La, not shown) are all strongly and

positively correlated between them ($r>0.977$, Table 1). Consequently, the lithophilic inter-element ratios are stable for all samples and do not differ for more than a factor of 2.2 from those calculated based on the average values for the upper continental crust proposed by Wedepohl (1995).

The Zn, Cu and Pb profiles are similar, especially below 14 g cm-2, closely following the TiO_2 variations (Figure 3). The Zn, Cu and Pb profiles present maximum values at mass depths ranging between 1.2 and 1.8 g cm-2: 139, 18 and 39 - g g-1, respectively, and tend to decrease upward.

Concerning the lowest values recorded, the maximum values correspond to a slight but significant enrichment of 2.7 for Cu and 4-5 for Pb and Zn. The 206Pb/207Pb ratios remarkably mirror the Pb concentrations, with values ranging between 1.154, Pb concentration peaks, and relatively steady 1.21-1.22 values below a mass depth of 13 g cm-2. Total
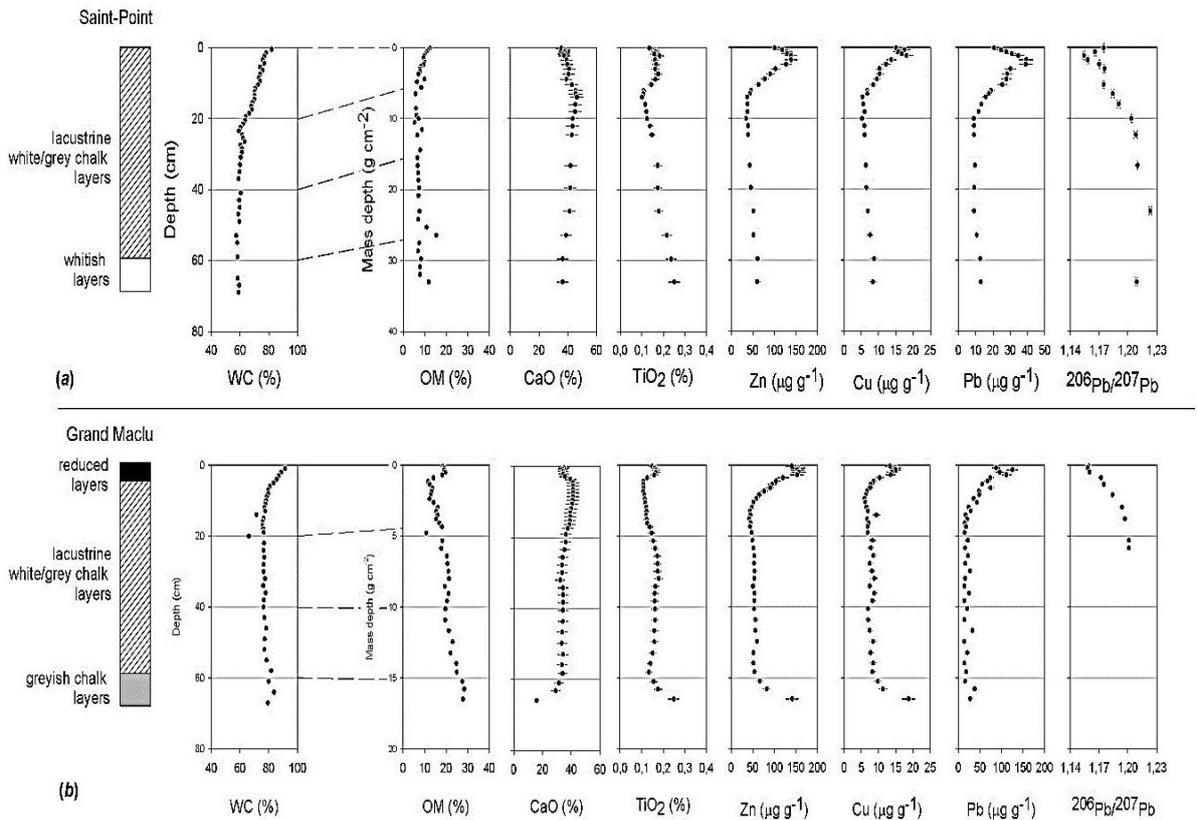

Fig. 2. Core log, water and organic contents, CaO, TiO2, Zn, Cu, and Pb concentrations, and 206 207 Pb/ Pb ratios for Saint-Point (a) and Grand Maclu (b)

Table 1. Pearson's correlation coefficients between lithophilic elements in the upper half matrix for the Saint-Point lake sediments

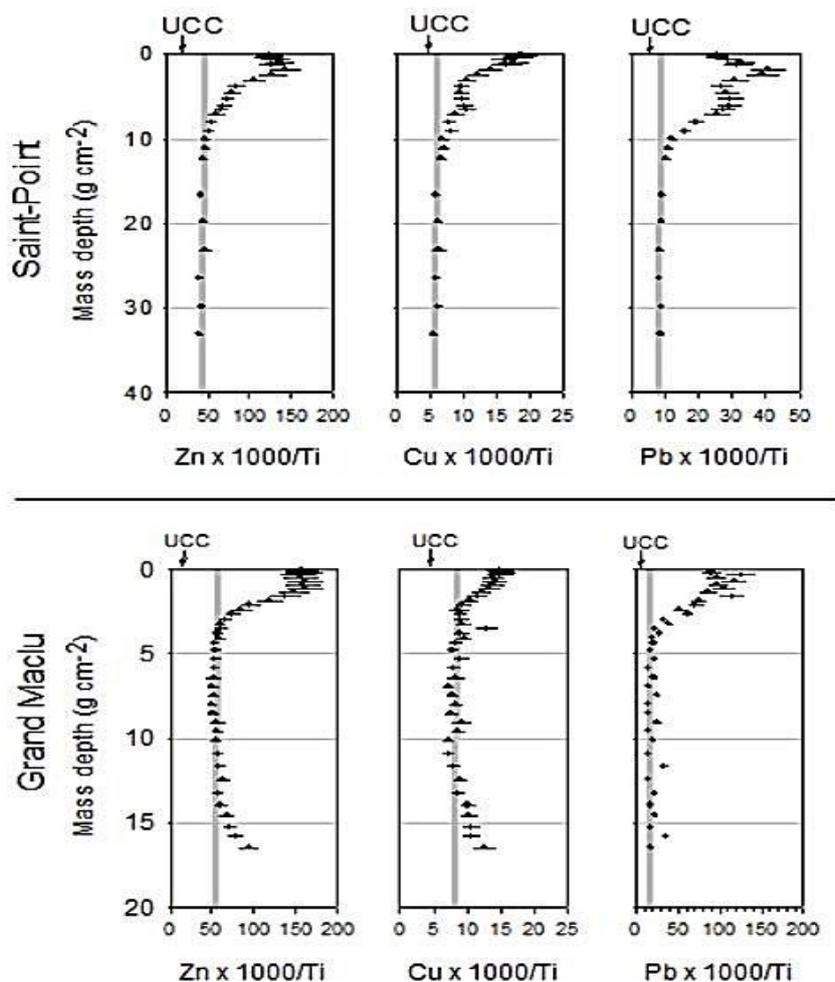|	La	Th	Zr	Al	Ti
La		0.996	0.989	0.991	0.990
Th	0.32 [0.31]		0.986	0.981	0.982
Zr	3.4 [7.3]	11 [23]		0.977	0.986
Al	1500 [2400]	4600 [7500]	430 [330]		0.987
Ti	84 [96]	260 [300]	24 [13]	0.055 [0.040]	

Fig. 3. Zn, Cu and Pb profiles enrichment

$210Pb$ and $210Pbinsitu$ assumed to be in secular equilibrium with $214Pb$, are depicted in Figure 4a. 210 Pbinsitu appeared to be reasonably constant along the sequence (44 ± 8 Bq kg-1). The total $210Pb$ exponentially decreases downward from 290 Bq kg-1 at the sediment-water interface and reaches the values of the $210Pbinsitu$ around a mass depth of 6 g cm-2. The $137Cs$ exhibits two clear peaks

of 114 and 152 Bq kg-1 at mass depths of 1.2 and 2.4 g cm-2, respectively. The $241Am$ is significantly non-null (1.9 Bq kg-1) only at a depth of 2.4 g cm-2.

Geochemical and radiochemical results for Grand Maclu

OM content regularly decreases from about 28 % at the bottom of the core to 12 % at a mass depth of 1.4 g cm-2, from

where it slightly increases. At first glance, the observations done for the CaO and the lithophilic elements from the Saint-Point core are valid for Grand Maclu (Figure 2, Table 2). While some lithophilic inter-element ratios are similar (for instance, Ti/Th and Th/La), some others are very distinct (Al/Zr and, to a lesser extent Al/Th), suggesting that non-carbonaceous mineral matter involved is, at least in part, of different origin. Moreover, a drastic increase of terrigenous-derived material (see TiO_2 profile in Figure 2) is noticed from a mass depth of 15 g cm-2 to the bottom. Zn and Cu concentrations mimic TiO_2 up to 17-18 g cm-2 mass depth and

then increase out of proportion toward the top of the sequence.

Pb content is relatively steady below 4 g cm-2 (~20 µg g-1) and rises upward. If the bottom of the sequence is disregarded, the highest Zn, Cu and Pb concentrations are recorded at 0.35 g cm-2 mass depth. That corresponds to an enrichment, calculated using the lowest concentrations as a reference, of 3.7, 2.5 and 9, respectively. $206Pb/207Pb$ ratios vary from 1.16 at the top to 1.20 at 5.3 g cm-2; the deepest sample measured for lead isotopes. Similarly to the Saint-Point core, the $210Pb_{insitu}$ is relatively steady at 46 ± 8 Bq kg-1 (Figure 4b).
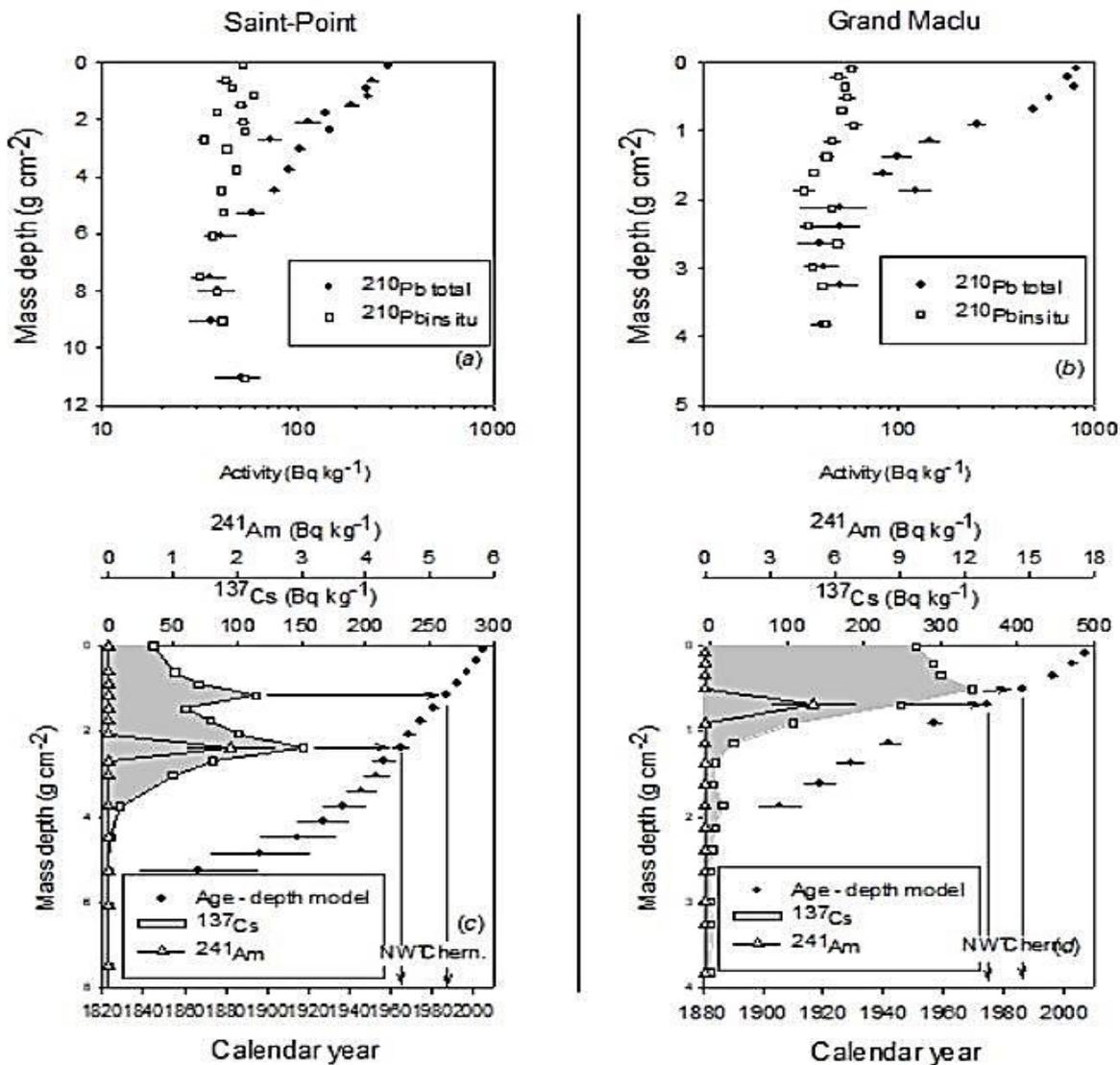

Fig. 4. Evolution of total ^{210}Pb, ^{210}Pb$_{insitu,}$ ^{137}Cs and ^{241}Am activities (in Bq kg^{-1}) in depth (expressed in g cm^{-2}) for Saint-Point (a) and Grand Maclu (b)

Table 2. Pearson's correlation coefficients between lithophilic elements in the upper half matrix for the Grand Maclu lake sediments

	La	Th	Zr	Al	Ti
La		0.994	0.959	0.995	0.975
Th	0.30 [0.31]		0.959	0.991	0.975
Zr	2.5 [7.3]	8 [23]		0.947	0.988
Al	2000 [2400]	6700 [7500]	751 [330]		0.975
Ti	73 [96]	240 [300]	29 [13]	0.035 [0.040]	

The total ^{210}Pb presents high values near 800 Bq kg-1 within the first 0.35 g cm-2 horizons and declines up to the activity of the ^{210}Pbinsitu at 2.2 g cm-2. 137Cs starts growing from 1.1 g cm-2. Unlike the Saint-Point core, one single peak of about 340 Bq kg-1 is observed at 0.5 g cm-2. The sole non-null value of 241Am is recorded below, at 0.7 g cm-2.

Chronology of the cores

Before establishing dating, it is noteworthy that average ^{210}Pbinsitu activities of 44 ± 8 and 46 ± 8 Bq kg-1 determined respectively for the Saint-Point and Grand Maclu lakes, are pretty similar to those previously measured in carbonaceous-dominated sediments of the Geneva lake at two places, which provided averages of 40 and 50 Bq kg-1 (Monna *et al*., 1999). Moreover, the atmospheric 210Pb fluxes, calculated by multiplying the 210Pbxs inventory by the disintegration constant, yield similar values of ~ 150 and 170 Bq m-2 yr-1 for Saint-Point and Grand Maclu, respectively. Such values are remarkably consistent with atmospheric fluxes of 150 ± 3 Bq m-2 yr-1 measured by Caillet *et al*. (2001) at Versoix, close to Geneva, 40-60 km away.

Saint-Point. The two well-resolved peaks of 137Cs activity, at mass depths of 2.4 and 1.2 g cm-2, almost certainly record the 1962/63 fallout maximum from the atmospheric testing of nuclear weapons, and presumably, the fallout from the 1986 Chernobyl accident (already detected nearby, in the Geneva lake, Monna et al., 1999; Dominik, 1981), respectively, all the

more that traces of 241Am coincide with the most profound 137Cs peak (Figure 4a). The non-monotonic feature of ^{210}Pb between 2 and 3 g cm-2 may illustrate an episode of rapid accumulation, possibly due to an event such as a sediment slump. In many cases, the ^{210}Pb dates computed using the CRS dating model (Appleby *et al*., 1978) are in excellent agreement with the 1986 and 1963 depths determined independently from the 137Cs record. The 210

Pb-derived age model suggests a slow but steady increase in accumulation rates during the past 150 years, from around 0.021 g cm-2 yr-1 in the late 19th century to 0.067 g cm-2 yr-1 during the past ten years.

Grand Maclu. The relatively steep decline in 210Pbxs activity within the first 2 g cm-2 (Figure 4b) suggests that sedimentation at this site has been relatively slow (average of ~0.018 g cm-2 yr-1 over the past 100 years), while the almost uniform concentration in the top 0.35 g cm-2 of the core may indicate a recent acceleration in the accumulation rate. The well-defined peak 137Cs activity recorded at the mass depth of 0.5 g cm-2 probably corresponds to the fallout from the 1986 Chernobyl accident. Traces of 241Am detected at 0.7 g cm-2 suggest that sediments at these depths record the maximum 1963 fallout from the atmospheric testing of nuclear weapons (Appleby *et al*., 1992). The absence of a separate 137Cs peak recording the 1963 fallout maximum at this depth is presumably due to the low resolution of the 137Cs record caused by the slow

accumulation rate and probably the downwards migration of the 137Cs Chernobyl deposition. In many cases, the 137Cs Chernobyl peak of 1986 is in good agreement with the age-depth model based upon the CRS model.

Anthropogenic contributions

The measured total concentrations and isotopic compositions can be divided into two parts: the component coming from the natural background and, in addition, the anthropogenic inputs. Several approaches have been developed to complete the first step, which consists of isolating the human-derived contributions. Besides leaching-based procedures (refs), which are known as suffering from a lack of selectivity (refs), the normalization of metallic contents, supposedly at least in part of anthropogenic origin, by a conservative lithophilic element (such as Sc, La, Al, Ti, or Zr, refs) tends to win overall recognition. Then, the excess metal contribution can be assessed by using the following equation:

$$M\text{excess} = M\text{total} - L \times (M/L)\text{natural} \quad (1)$$

Where Mtotal represents the total metal M concentration; Mexcess, the excess contribution to the total concentration; L is the total lithogenic element content, chosen here as a surrogate for natural mineral matter; (M/L) natural is supposed to be constant and corresponds to the ratio between the metal M, and the lithogenic element L contents in pre-anthropogenic conditions. Here, La, Zr, Th, Al, and Ti are positively and highly correlated in each of the cores (Table 1-2), so that any of these elements will produce the same results in terms of anthropogenic delineation. However, the differences observed between lithophilic inter-element ratios in the two cores (Tables 1-2) suggest that the nature of the non-carbonaceous mineral matter is not strictly identical. Consequently, the same (M/L) natural ratio value cannot be used for both Saint-Point

and Grand Maclu sequences. Hence, taking values assessed for the upper continental crust is not a good idea because they can only be considered mean values, which do not reflect the local situation, especially divergences observed between both cores. An alternative consists of taking as reference values for (M/L) natural ratios, the deepest samples that should ideally correspond to pre-anthropogenic levels. All the profiled metals showed a relative increase in their levels, similar to the two lakes' lead profiles (Grand Maclu and Saint-Point). This recorded increase is marked by an enrichment factor of > 2 for several metals (excesses), suggesting a solid contribution from external anthropogenic sources. The comparison with the lead profiles confirms these remote origins, particularly during the second half of the 20th century.

Levels thus rose from 50 ppm, 10 ppm respectively for Zn and Cu to reach their maximum in the late 1960s (150 and 20 ppm). The apparent decrease of these levels in the first few centimetres of sediments cannot be solely attributed to decreased external inputs but the chemical exchanges at the water-sediment interface. These exchanges cause the passage of a fraction of interstitial waters (and their associated chemistry) into the free water mass under redox conditions during periods of direct stratification (Figure 5).

CONCLUSION

The study's carried out results on the Jura lakes confirm the extrinsic origin of these metallic inputs that were found to be mostly of industrial origins. The local contribution is minimal, or even absent, thus highlighting the positive effects of the lakes' managers' actions in response to the successive French laws (1992 Law; 2006 Law). Nevertheless, the geochemical profiles of the principal heavy metals recorded in the sediments and, to a lesser extent, in the interstitial waters confirm that the external inputs closely follow the
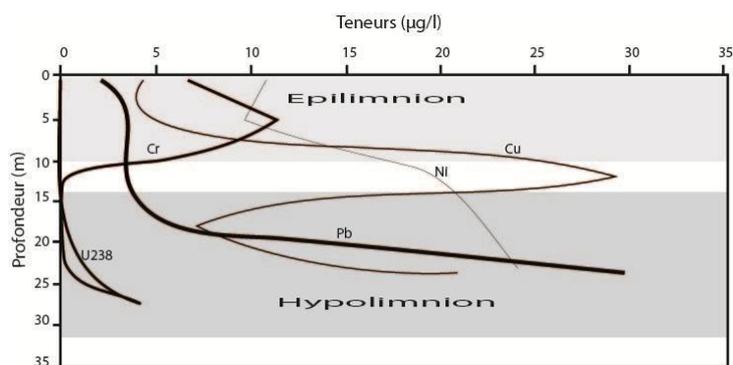
Fig. 5. Heavy metal content in free water mass during the stratification

lead profiles. The latter's isotope ratios also indicate its extrinsic origins, thus confirming the possibility of atmospheric inputs from several volatile heavy metals.

The calculated excess of metals shows a rise from the end of the 19th century. This increase reached its peak in the 1960s and 1970s, reflecting the industrial acceleration that Europe experienced after the Second World War. Indeed, industrial development has strongly contributed to the multiplication of heavy metal sources, which increased the level of many heavy metals in the environment. Thus, Zn is the most critical input, followed by Cu and Pb. The same rule applies to other elements such as Hg and Cr. Prolonged anoxic conditions for more than 5 months during stratification phases may probably ensure favourable conditions for chemical reactions that can produce relatively toxic compounds.

It is therefore advisable to further investigate the nature of exchanges between both water and sediment on the one hand and between pore water and open water on the other and to assess the input of organic matter and its consequence on the oxygen content at depth during the stratification period of these dimictic water bodies. The particulate component undoubtedly plays an important role that could give a precise idea of the external inputs from the catchment area, thus making it possible to establish a balance and identify the periods during which the lakes pass from a sinking state to a source state and thus to pinpoint the release

phases and above all the chemical compounds emitted.

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