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Research Article

Multi-Secular Lead (Pb) Contamination on a Regional Scale: Comparative Analysis of the Grand-Maclu and Saint-Point Lakes in the Jura Area, France

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Abstract For nearly a century, the lakes in the Jura area (France), as for those throughout the northern hemisphere, have been impacted by heavy metal contamination. The Jura lakes were considered as long protected and undisturbed owing to the agricultural and rural nature of their catchment areas and thus the lack of anthropological impacts. Meanwhile, chemical analysis of sediments of some of these lakes and in particular, the Grand-Maclu and Saint-Point lakes, has indicated that in fact these lakes have not escaped contamination. The levels of lead measured in the top 20 centimeters (EF $>$ 2) have revealed that the source of the metal contamination originates from outside the catchment area. The thickness and the depth of these sediments correspond to the 1870–2005 period and the results highlighted the direct impact of the industrial activities that developed during the end of the 19th century in Europe, and more generally in the northern hemisphere. The chemical analysis results of the two lakes, having very different geographical and demographical characteristics, have confirmed the presence of lead contamination and showed that the differences in the measured lead amounts resulted from geographic factors such as the catchment area and its relief, water renewal rate and vegetation.

Keywords pollution; lakes; isotopes; lead; Jura; catchment area; sediments

1 Introduction

The impact of industrialization on the environment, in the northern hemisphere, has been reported in several publications (Bindler et al. [11]; Brooks et al. [17]; Boyle et al. [12, 13, 14, 15]; Brugam et al. [18]; Ariès [7], Hynyen et al. [22]; Kamenik et al. [24]; Landmeyer et al. [26]; Renberg et al. [11, 19, 30]; Tait and Thaler [35]; Weiss et al. [36]). The sediments present in lakes and wetlands provide excellent environmental records and their analysis has confirmed the abnormally high content of several heavy metals dating back to 1870. This date corresponds with the beginning of industrial activity in the northern countries. Traces of lead, copper and other heavy metals have been detected in several lakes dating back to Medieval and Roman times (Arnaud [8]; Shotyk et al. [33]). Anthropological impacts over the last two centuries can account for over 90% of the contaminants found in the vast majority of the investigated lakes (Norton et al. [29]; Jackson et al. [23]). The rate of lead input steadily increases up to the 1970s, corresponding to the period where the use of lead as lead tetraethyl in gasoline was phased out. The sediments dating back to the period after the 1970s show a gradual reduction in lead contamination (Arnaud et al. [8, 9]; Shotyk et al. [33]). The amount of Pb in the sediments varies as a function of three factors: (1) geographic (prevailing wind exposure, altitude, size of catchment area), (2) hydroclimatic (input discharge to lake, rainfall, water renewal time), and (3) ecological (peri-lacustrine peat deposit belts, humid zones within the catchment area, organic layer thickness) (Nedjai et al. [27, 28]). Atmospheric fallout is not the only vector of lead contamination to the lakes, the geographical characteristics and the anthropological activities carried out within the catchment area also constitute a source of contamination. Indeed, the lakes of the alpine valleys exhibit disturbances in their lead profiles, indicating that local sources add to the sediment contamination already present (e.g., Lac du Bourget). The French Jura area is characterized by its agricultural activities (particularly in the plateau zones) and by the very low industrial activity (in particular steel and coal works). *Some* of the lakes are considered to have a small size with catchment basins surface areas around 100 hectares. Few residences have been built in these areas and thus discharged relatively small amount of wastewater in the lakes. These lakes are characterized by a predominantly arboreal vegetation cover (conifers and deciduous). The

Grand-Maclu lake belongs to this category of small lakes and was selected for investigation. Its analytical data were used as representative of small size lakes and for comparison with results obtained from large size lakes such as the Saint-Point Lake. Indeed, Saint-Point lake belongs to the category of Jura large-size lakes where impacts from tourist activity are considerable. This economic activity has been accompanied by an important urban development and by the setting up of a number of industries. All of those human and industrial activities constitute a potential source of pollution. The presence of a public dumping in the catchment basin and more precisely nearby the Saint-Point lake could constitute a source of production and intake of lead into lake. In order to check this eventual contribution, water samples within the public dumping were taken for quantitative determination of ^{206}Pb, ^{207}Pb and ^{208}Pb isotopes. Its atomic ratios values of ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb were compared with those of lacustrine sediments.

The two above-cited selected lakes represent all situations that are encountered in the Jura area about heavy metal contamination. Indeed, the Saint-Point lake, with its large size, collects all water flowing throughout a very large catchment basin with forest and very anthropogenic (high residence and population density, important industrial infrastructure with numerous humid zones) dominant. Conversely, the Grand-Maclu lake, with its small size (some hectares) and located at the beginning of the basin, could be considered as reference lake. Its catchment basin is not subject to any pressure of anthropogenic origin. The dominant vegetation is essentially arboreous (leafy, resiniferous). Unlike the Saint-Point lake, the Grand-Maclu lake is not affected by any intake of anthropogenic origin that could alter its water quality.

It is, however, the existence of a landfill, in proximity to the lake, which receives the most criticism with regard to potential lead contamination. We will attempt, via the analysis and comparison of lead found in the two lakes, (1) to identify the source of the lead production via isotope dating; (2) to determine the evolution of the amount of lead over nearly the last three centuries; and (3) to highlight the contribution of industrial activities and to estimate the anthropological influence in the lead contamination process since the mid-19th century. The comparison of lead amount present in the two above-cited lakes is also used to verify previous hypotheses on external or internal origin of lead.

2 The geographical location of the present study

The Grand Maclu and Saint-Point lakes are located in the Jura and the Doubs areas respectively. More precisely, their geographical coordinates are: 46°37’52 longitude and 5°54’56 latitude and 6°18’50 longitude and 46°48’55” latitude respectively (Figure 1). Their average altitudes are approximately 800 m and 850 m respectively. Both lakes have an elongated form following a north-south axis (N 10°). Of glacial origin, they occupy morphological depressions, formed from a single basin for the former and two basins for the latter. Their maximum depths are respectively 15–20 m and 38 m and their surface areas are 1.02 km^2 and 5.2 km^2 respectively.

Located at the head of the large Herisson catchment basin, the Grand Maclu catchment drains a small surface area of 1.13 Km^2. Conversely, the Saint-Point lake is fed by the Doubs river which drains a catchment of approximately 7710 km^2.

The geology of the two lakes is quasi-identical, marked by a predominance of carboniferous formations (limestones and muddy limestones with occasional sandstone strata) which are essentially of Jurassic and Cretaceous age. These formations are locally connected by morainic formations which blanket the lake basins. Alternating layers of marl and limestone intersperse the layers of Jurassic limestone. Occasional spots of molassic formations are found lying in unconformity with the older formations.

These formations are characterized by a high degree of karstification giving them a good permeability and rate of through-flow towards the lake basins. Several springs punctuate the contact zone between lake and basin. The rapid rise in water level in the two lakes shorten their water renewal time of less than 12 months. The regional climate is continental with a strong oceanic influence and a west-southwest prevailing wind. Precipitation occurs mainly as rainfall during the stormy spring and autumn seasons but also as snow during winter. The average precipitation rate varies in the range 2,000–2,200 mm.

3 Methodology

Sediments sampling were carried out at locations indicated by a bathymetric map, which was drawn using a Syqwest echo sounder. This device provides data on sediment depth. The involved sampling at three selected sites, with gentle slopes and little-disturbed deposits, for borehole coring. Sediment coring was carried out using two meter plexiglass tubes with double hermetic corking. Samples were then taken to a depth of 70 cm, representing approximately 300 years of history (see chronology). After extraction, the borehole core samples were directly brought to the laboratory for treatment according to the protocol as follows:

3.1 Sediment sampling

– 1 cm *thickness* samples were taken at the first 20 cm depth level *which is considered as representative of the whole time period affected by industrial emissions*. 2 cm *thickness* samples were taken at a level between 20 this sediment layer corresponds to the preanthropogenic

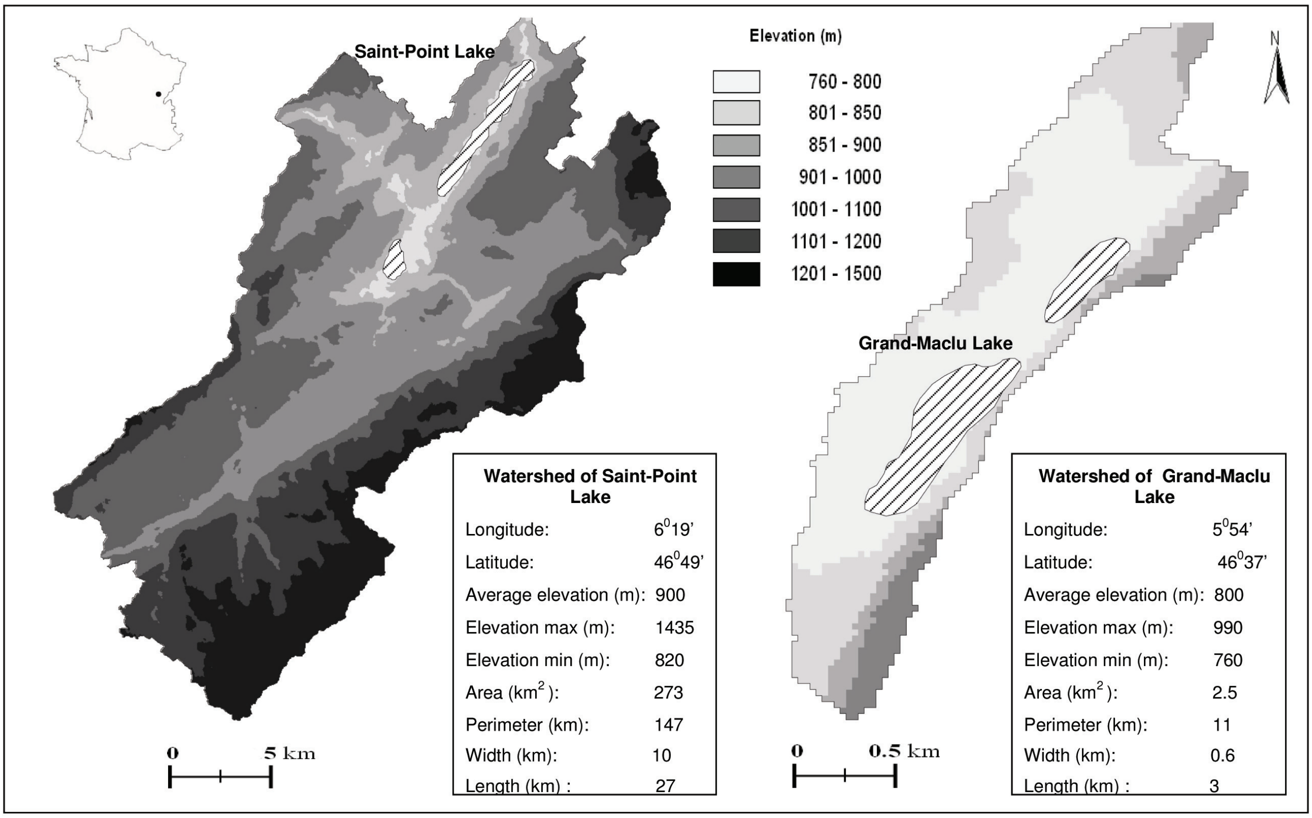

Figure 1: Location of the Grand-Maclu and Saint-Point lakes (Jura, France).

period and 40 cm depth and finally, 3 cm *thickness* samples were taken at *a level* between 40 and 70 cm depth this sediment layer should be free of anthropogenic activities.

- Each sample was stored in two polyethylene tubes and subsequently frozen.
- The samples were lyophilized after sieving. Selected sediment fine powder sample was used for geochemical and isotopic characterization; and organic matter determination. Isotopic data obtained from above cited analysis were then used for lead (Pb210) and cesium (Cs137) dating.

3.2 Quantitative elementary analysis using the ICP-MS technique at the analytical laboratory (CRPG, Vandoeuvre-les-Nancy, France)

The following protocol was used for the heavy metal analysis:

- Melting of a mixture of 200 mg of rock with 600 mg of lithium metaborate in crucibles (automatic tunnel oven), followed by dissolution of melted samples in 1N nitric acid. The mass proportions of the two compounds in the rock:mix ratio could be modified according to the type of sample.
- The nitric acid solution containing a sample was then analyzed for quantitative determination of major and minor elements using ICP-AES technique and 43 trace elements using ICP-MS technique
- Calibration for quantitative ICP-MS measurements is done using geochemical standards or appropriate environmental sample. The latter receives similar treatment to that of general samples and is doped with some determined trace elements.

3.3 Chronology and isotopes

Isotope analysis consisted of ^{210}Pb and ^{137}Cs dating, in a laboratory of Department of Mathematical Sciences in Liverpool (UK), according to the protocol as follows:

Dried sediment samples from the Grand Maclu Lac core GMAC07/1 were analyzed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am using direct gamma assay in the Liverpool University Environmental Radioactivity Laboratory using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby et al. [3]). ^{210}Pb was determined via its gamma emissions at 46.5 keV, and ^{226}Ra by the 295 keV and 352 keV γ-rays emitted by its daughter radionuclide ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs

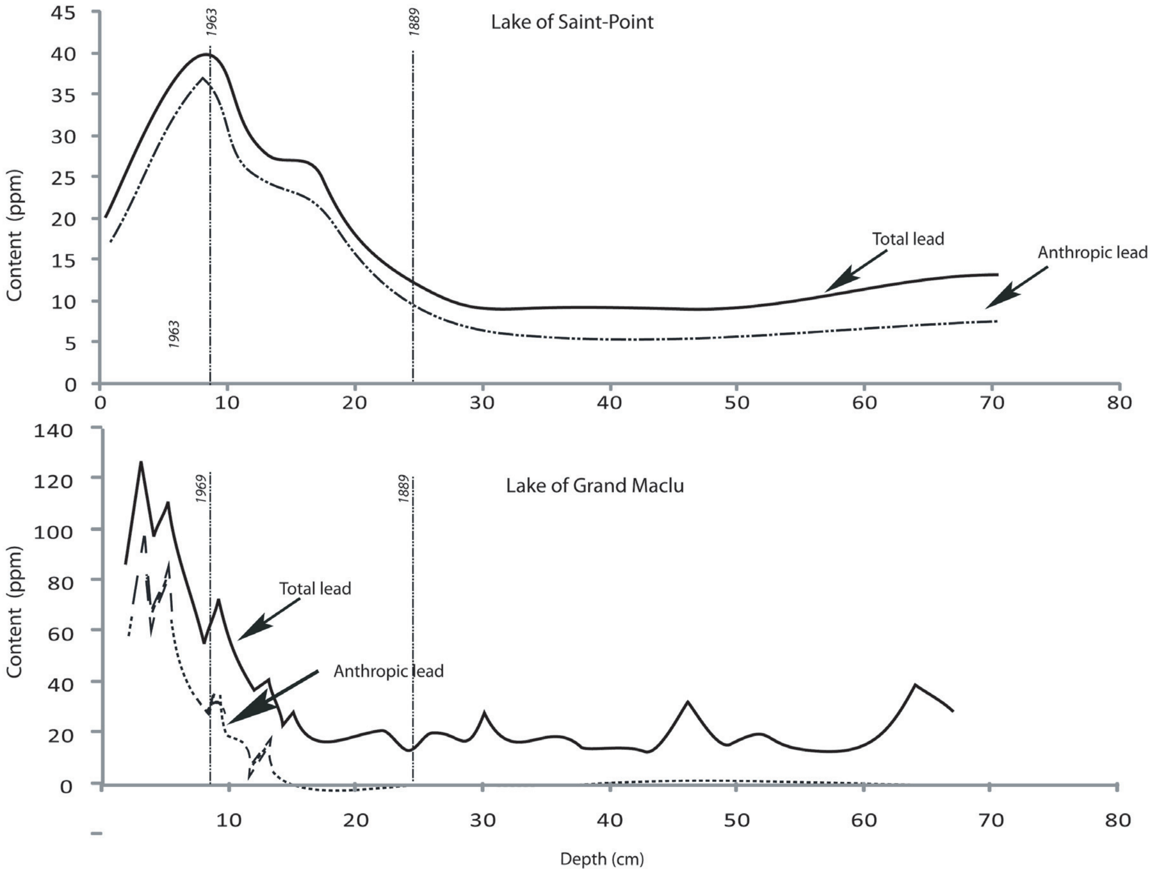

Figure 2: Lead concentration profiles over a thickness of 70 cm, in the sediments from Grand Maclu and Saint Point Lakes.

and ^{241}Am were measured by their emissions at 662 keV and 59.5 keV respectively. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy γ-rays within the sample (Appleby et al. [6]).

This dating method provided data going back to the 1880s, signaling the beginning of industrialization. The estimated sedimentation rate was used to lengthen the study period by extrapolation in accordance with the results obtained by Shotyk et al. [33] and Arnaud et al. [9].

Ten samples were selected for determination of lead isotopes amounts at the "Geochemistry Laboratory" in Heidelberg (Germany). Pb206 and Pb207 isotopes were analyzed according to a method described by Krachler et al. [25]; Bell et al. [10].

4 Results and discussion

4.1 Evolution of the lead deposition in the two lakes

Results obtained for lead analysis in the two core samples from the above cited lakes have indicated very similar trends from the base of the core up to 10 cm. For the upper part of the core samples displayed in the graphs of Figure 2, the lead profiles show three types of trends corresponding to three depths as follows:

4.1.1 Sedimentary surface level

Between 0 and 7 cm depth, the lead profiles for the two lakes are very different: the Saint-Point lake profile is characterized by very low lead concentration (< 40 ppm) whereas the Grand Maclu profile shows an irregular variation for lead concentration. Indeed, and an unexpected significant increase of lead concentration was observed from 40–45 ppm in 1970 to over 140 ppm in 2005. The Saint-Point lake profile remains within the pattern recorded in the other lakes of the region, showing a gradual decrease of lead concentration from 39–40 ppm in the middle of the 1970s to approximately 20 ppm at the surface (2005) (Nedjai et al. [27]).

4.1.2 Sedimentary middle level

The middle level corresponds to the depth interval between 7 and 22 cm which covers the period dating from 1870 to 1970. These dates have been found to be the key in the vast majority of studies carried out on lakes in the northern hemisphere. The 1970s are marked by the reduction in lead concentration present in the atmosphere which results from the phasing out of leaded gasoline. From 22 cm up to 6–7 cm (1970), the lead concentrations significantly and steadily increase up to the maximum value of 140 ppm for the Grand-Maclu lake and 40 ppm for the Saint-Point lake. Several studies have confirmed the influence of industrial emissions (coal and steel works) in northern Europe as well as hydrocarbon emissions (particularly gasoline) since the 1920s and 1930s when lead was introduced as an additive to gasoline in the United States of America and Europe, respectively.

The increase in lead levels did not begin at the same time for the two lakes. For the Grand-Maclu lake, the lead concentration starts to increase only at the beginning of the 20th century. Conversely, the lead concentration increase in the Saint-Point lake was observed since the end of the 19th century. The late absorption of lead by the Grand-Maclu lake is probably due to the small surface of its catchment basin and its weak exposition to dominant winds coming from ocean. Conversely, the Saint-Point lake, relatively larger than the Grand-Maclu lake, is characterized by its location at high altitude and its exposition in favor of west winds.

4.1.3 Sedimentary lower level

Below 22 cm, the profiles for the two lakes show an identical configuration, corresponding to natural influxes to the lakes. The lead levels recorded for both lakes are close to the geochemical background and fluctuate around 6–7 ppm.

The large amount of lead determined in the Grand-Maclu lake is probably due to hydrogeographical factors such as aspect, forest cover, hydrological fluxes and thus discharges. Indeed, the Saint-Point lake can be distinguished by markedly shorter turn-over times because it drains a larger catchment area. Conversely, the hydrological fluxes measured at Grand Maclu rarely exceed 0.5 m^3/s and may even run dry during 3 months in summer, transforming the lake into a closed system.

4.2 The origin and intensity of lead contamination

The determination of enrichment factors (EF) associated with lithology allowed to confirm the presence of lead pollution during the 1870–2005 period and to watch its evolution all along the length of the core. The EF at Saint-Point lake vary from the value 1 at the core base to 5 in 1963. The EF's value 1 is considered as representative of a lake unaffected by lead pollution. If the threshold fixed by Shotyk et al. [34] is taken as the lead pollution lower limit in the present work, the Saint-Point lake entered the lead contamination stage from early 29th centimeter which corresponds to the 1880–1890 period. This date coincides with the industrial revolution. This lead pollution phenomenon affected the Grand-Maclu lake only around the 15th centimeter. This value corresponds to the 1920–1930 period during which lead was added to gasoline at first, in the USA during the 1920 (Ariès [7]) and then in Europe during the 1930. At the Saint-Point lake, the lead pollution level has reached the maximum (40 ppm) in 1963. After this date, its started to slightly decrease and finally was stabilized around the value of 3.5 at the surface. The Grand-Maclu lake displays many disturbances in the EF values during the last thirty years. Thus, its EF values vary from 7.17 in 1969 to 5.88 in 2000. Under this condition, the high lead content at the surface led us to assume a local contamination probably from underground contributions. Indeed, The presence of a small village on the plateau of Haut (Chaux du Dombief) implies that human activities could generate urban dumping and contribute to increase the lead pollution level. Meanwhile, this hypothesis could not be confirmed since the sampling has been carried out at a location above the lake and far from the area susceptible to be affected by those eventual pollutions. An error in analysis is possible, knowing that a second sampling at the location close to that of the present study has been performed by the organism "Agence de l'eau RM&C, 2004" and its analysis did not point out any anomaly (see Table 1).

These observations clearly indicate that the lead pollution mainly result from anthropologic activities since the end of the 19th century. Calculations show that human impact accounts for around 85% of the influx during the 1870–1970 period (Figure 2).

The results of the isotopic analysis, obtained from 20 samples taken from the two cores, allow to make three observations (Figure 3):

- From the base of the two cores up to 22 cm (1870), the ($^{206}Pb/^{207}Pb$) lead isotopes ratio varies in the range 1.22 and 1.20. This variation confirms the natural origin of the lead found at this depth.
- Similar values of lead isotopes ratio have been found at the Gruyère pond in Switzerland (Shotyk et al. [33]) as well as in the Pyrenees (Ariès [7]). They confirm natural origin of lead contributions (background).
- The same lead isotope ratio gradually decreases and reaches the value 1.15 in the 1970s. This can be interpreted as an indication of lead production of anthropological origin. This result as well as those of Gruyere pond (Switzerland), Pyrennées (France) (Ariès [7]) and in Sweden (Shotyk et al. [25]) confirm the anthropologic origin and more exactly industrial origin with lead emission. The inflexion recorded in the middle of the 70 is the fact of particular importance on the decrease of lead contributions due to the reduction of lead addition in gasoline.

Date	Depth (cm)	Pb ppm	Pb Nat. ppm	$Pb_{An}t$ ppm	EF	$^{206}Pb/^{207}Pb$
2005	1	20.68	2.98	17.70	3.25	1.175
	2	24.59	3.56	21.03	3.28	
	3	27.79	3.60	24.19	3.39	1.166
	4	30.91	3.51	27.39	3.76	
	5	34.73	4.04	30.69	4.05	1.154
	7	39.29	3.58	35.71	4.98	1.158
1963	9	38.99	3.69	35.29	5.07	1.170
	11	30.16	3.60	26.56	4.15	1.175
	13	28.16	3.91	24.25	3.65	
	15	27.73	3.62	24.10	3.69	
	17	25.51	3.18	22.33	3.86	1.175
	19	18.97	2.41	16.56	3.83	
	20	17.64	2.39	15.26	3.46	1.184
	21	15.69	2.25	13.44	3.40	
1898	23	13.30	2.56	10.74	2.50	1.191
	25	11.60	2.70	8.91	2.01	
	27	8.92	2.76	6.16	1.56	1.204
	29	8.97	3.05	5.92	1.32	
	32	8.99	3.25	5.74	1.18	1.208
	40	9.50	3.85	5.65	1.16	1.210
	46	9.21	3.85	5.36	1.08	
	52	8.92	3.96	4.96	1.02	1.223
	58	10.49	4.80	5.69	1.01	
	64	12.63	5.24	7.39	1.00	
	70	12.92	5.55	7.38	1.00	1.209

(a) Lake of Saint-Point

Date	Depth (cm)	Pb ppm	*Pb Nat.* ppm	*Pb anth.* ppm	EF	$^{206}Pb/^{207}Pb$
2005	1	514.1	27.9	486.2	37.15	1.159
	2	87.6	27.9	59.7	5.88	1.158
	3	125.4	28.0	97.4	8.41	
	4	96.0	28.0	68.0	6.39	1.16
	5	111.6	27.9	83.7	7.74	
	6	73.9	27.8	46.1	6.24	1.172
	7	67.5	27.7	39.8	6.33	
	8	55.3	27.7	27.6	5.31	1.175
1969	9	74.9	27.7	47.1	7.17	
	10	47.9	27.7	20.2	4.60	
	11	48.3	27.7	20.6	4.45	1.184
	12	35.7	27.7	8.0	3.06	
	13	42.7	27.7	15.0	3.73	
	14	23.6	23.6	0.0	1.99	1.194
	15	28.6	28.6	0.0	2.40	
	16	16.9	16.9	0.0	1.37	
	17	20.4	20.4	0.0	1.64	1.197
	18	14.8	14.8	0.0	1.14	
	19	17.8	17.8	0.0	1.31	
	20	14.5	14.5	0.0	1.00	
	22	21.5	21.5	0.0	1.40	1.201
1898	24	15.4	15.4	0.0	0.92	1.201
	26	22.4	22.4	0.0	1.23	
	28	16.0	16.0	0.0	0.93	
	30	26.8	26.8	0.0	1.52	
	32	15.7	15.7	0.0	0.87	
	34	14.2	14.2	0.0	0.84	
	36	24.7	24.7	0.0	1.42	
	38	14.1	14.1	0.0	0.88	
	40	20.1	20.1	0.0	1.27	
	43	13.9	13.9	0.0	0.86	
	46	32.7	32.7	0.0	2.08	
	49	13.3	13.3	0.0	0.84	
	52	21.0	21.0	0.0	1.42	
	55	14.0	14.0	0.0	1.00	
	58	18.1	18.1	0.0	1.37	
	61	15.5	15.5	0.0	0.97	
	64	37.8	37.8	0.0	2.04	
	67	27.3	27.3	0.0	1.00	

(b) Lake of Grand Maclu

Table 1: List of major elements and isotopic data of the sediments of Grand-Maclu and Saint-Point lakes.

– A slight increase of lead isotope ratio from 1.15 to 1.18 is recorded at the surface indicating a return to normal state and a reduction in lead contributions of anthropological origin (gasoline).

4.3 Differences in contributions and records in the first 20 cm

As it has been noticed for the lead profiles of Grand-Maclu and Saint-Point lakes, a significant difference is observed in the first 10 cm, showing a contrast in lead concentration in the two lakes. While the Saint-Point lake clearly shows a reduction of lead concentration from 7 cm depth up to the surface, following a similar trend observed in Switzerland (Gruyère lake: Shotyk et al. [33]; Anterne lake: Arnaud [8]), the Grand Maclu lake displays a more variable trend marked by several peaks and ending with an unprecedented increase in the lead concentrations up to 450 ppm at the surface. Meanwhile, the unusually high value of lead concentration is probably due to a measurement error. The lead amount determined by the "Agence de l'eau, 2004" appeared to be realistic and is adopted in the present study.

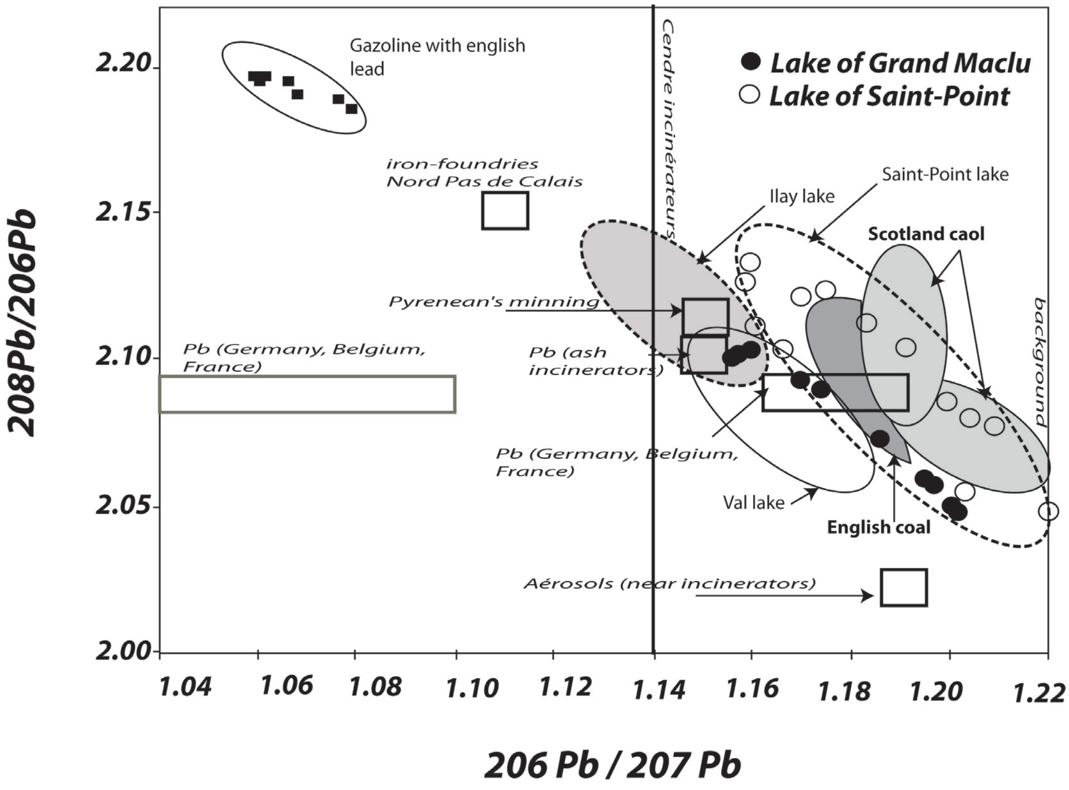

Figure 3: Comparison of the ($^{206}Pb/^{207}Pb$) lead isotopic ratios from the lakes in the present study with those from other European lakes (Shotyk et al. [25]).

The difference between lead concentration at the sediment surface of Grand-Maclu and Saint-Point lakes is larger than 100 ppm. Four hypotheses have been suggested to explain these differences:

- Westerly winds, of oceanic origin, could transport microscopic lead compounds and affect lakes facing west. The Saint-Point lake was not much affected by this type of lead pollution.
- A longer water renewal time for the Grand-Maclu lake (maximum discharges of some tens of liters/second) and thus a large surface area of contact between water and sediment have favored water-sediment interactions. This lake generally underwent a dry period over 4 to 5 months during summer. Under this condition, the water renewal was interrupted. Conversely, the Saint-Point lake drains a larger catchment area. Input and output water flows are permanent and much larger than the m^3/s.
- The presence of substantial peri-lacustrine peat deposits in the Grand-Maclu lake operates like a filter and precludes inputs of lead. The unabsorbed element could then dissolve in water if the water level is high enough to flood these zones. The large content of insoluble organic matter recorded in the Grand-Maclu and Saint-Point lakes confirm the filter role of these peat deposits.
- The presence of several ESE-WNW oriented faults, particularly at the south of the Grand-Maclu lake, may provide a drainage network for urban waste waters from neighboring villages which are located outside of the catchment basin and some kilometers from the lake at a higher altitude (850–900 m). However, this hypothesis appears to be improbable since the results obtained from isotopic analysis and in particular the $^{206}Pb/^{207}Pb$ ratio have indicated an increase from 1.15 at 6 cm depth up to 1.18 at the surface. The $^{206}Pb/^{207}Pb$ ratio values of the Grand-Maclu and Saint-Point lakes correspond to a high determination coefficient (R^2–0.49) (Figure 4) characterizing the common and external origin of the lead.

  The variation of periods corresponding to high and low levels of lead input to the Grand Maclu lake is probably originated from internal processes of the lake and its catchment area, such as the splitting of sedimentary sequences caused by sediment slides, a phenomenon confirmed by the dating of ^{210}Pb radioactive natural isotope.

  Local, urban inputs are almost absent in the Saint-Point lake despite the presence of a landfill (Labergement) in proximity to the lake.

  In order to check the eventual contribution of the dumping in the lake contamination by the lead, one water sample has been taken in the dumping site. This sample was analyzed for determination of three ^{206}Pb, ^{207}Pb and ^{208}Pb stable natural isotopes at the Geochemistry Laboratory (Heidelberg, Germany). Results obtained have indicated that the two ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios values are 1,1382 ± 0.0006 and 2,1342 ± 0,0015, respectively. These data are quite different from those recorded at the sediment surface of Grand-Maclu and Saint-Point lakes. The method used in the present study (a) to identify the sources of pollution and (b) to better determine the noncontribution of the dumping in the contamination process is suggested by Ek and Renberg [19]. It is based on the comparison of lead isotope concentrations of three different samples: (1) sample from the first centimeters of the sediments, (2) sample free of external lead contribution and (3) sample from the dumping's water. Results obtained from the lead isotope comparison allow to confirm or to infirm the role of the dumping in the lake contamination by lead. It also allows determining the origin of lead contribution.

Application of the two formulas to the sites at Saint-Point gives the following results:

$$^{208}\mathrm{Pb}/^{206}\mathrm{Pb}_{\mathrm{excess}} = \frac{(\mathrm{Pb}_{\mathrm{samp.}} * ^{208}\mathrm{Pb}/^{206}\mathrm{Pb}_{\mathrm{samp}}) - (\mathrm{Pb}_{\mathrm{bg.}} * ^{208}\mathrm{Pb}/^{206}\mathrm{Pb}_{\mathrm{bg.}})}{(\mathrm{Pb}_{\mathrm{samp}} - \mathrm{Pb}_{\mathrm{bg.}})}. \quad (1)$$

The amount of lead from the hypothetical source of contamination, the dumping, can then be determined by the equation (2):

$$\mathrm{Pb}_{\mathrm{cont.}} = \frac{\left(\dfrac{\mathrm{Pb}_{\mathrm{excess}} * ^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}_{\mathrm{excess}}}\right) - \left(\dfrac{\mathrm{Pb}_{\mathrm{excess}} * ^{206}\mathrm{Pb}}{^{208}\mathrm{Pb}_{\mathrm{Europe}}}\right)}{(^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{dump}} - ^{206}\mathrm{Pb}/^{208}\mathrm{Pb}_{\mathrm{Europe}})} \quad (2)$$

with:

$\mathrm{Pb}_{\mathrm{bg}}$: lead of sample taken from the bottom and free of anthropologic contributions;
$\mathrm{Pb}_{\mathrm{dump}}$: lead of dumping's water;
$\mathrm{Pb}_{\mathrm{samp}}$: lead of the sample;
$\mathrm{Pb}_{\mathrm{excess}}$: lead in excess;
$\mathrm{Pb}_{\mathrm{Europe}}$: European isotopic lead signature;
$\mathrm{Pb}_{\mathrm{Cont}}$: part of lead due to contamination by the dumping.

The use of the two equations (1) and (2) to calculate the lead isotopes ratios in samples taken from the Saint-Point lake provide results as follows:

Sample N°1: Surface core

$$\mathrm{Pb}_{\mathrm{excess}} = (\mathrm{Pb}_{\mathrm{samp}} - \mathrm{Pb}_{\mathrm{bg.}}) : 20.68 - 12.92 = 7.76\,\mu\mathrm{g/g},$$
$$\mathrm{Pb}_{\mathrm{excess}} = (\mathrm{Pb}_{\mathrm{samp}} - \mathrm{Pb}_{\mathrm{bg.}}) = 34.9.$$

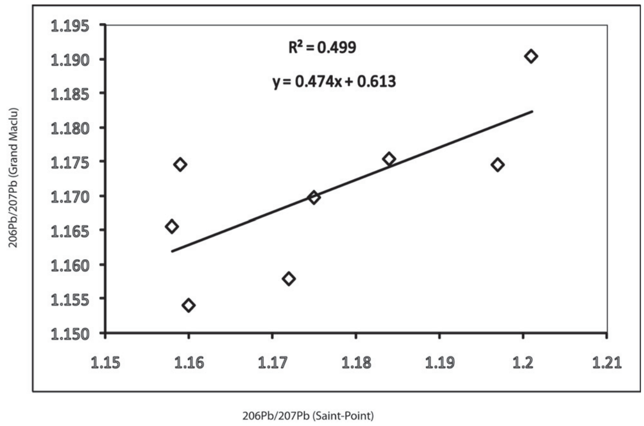

Figure 4: Correlation of ^{206}Pb/^{207}Pb stable natural isotope ratios for Saint-Point and Grand-Maclu lakes.

Based on data from Saint-Point:

$$^{208}\mathrm{Pb}/^{206}\mathrm{Pb}_{\mathrm{bg}} = 1.22, \quad ^{208}\mathrm{Pb}/^{206}\mathrm{Pb}_{\mathrm{dump}} = 1.13,$$
$$^{208}\mathrm{Pb}/^{206}\mathrm{Pb}_{\mathrm{Europe}} = 1.17, \quad \mathrm{Pb}_{\mathrm{excess}} = 21.81,$$
$$^{208}\mathrm{Pb}/^{206}\mathrm{Pb}_{\mathrm{excess}} = (20.68 * 1.17) - (12.92 * 1.209)/(7.76) = 1.10438,$$
$$\mathrm{Pb}_{\mathrm{dump}} = (7.76 * 1.104) - (7.76 * 1.17)/(1.13 - 1.17) = \sim 0\,\mu\mathrm{g/g}.$$

Sample N°5: depth 5 cm

$$^{208}\mathrm{Pb}/^{206}\mathrm{Pb}_{\mathrm{excess}} = (34.73 * 1.15) - (12.92 * 1.209)/(21.81) = 1.29,$$
$$\mathrm{Pb}_{\mathrm{dump}} = (21.81 * 1.29) - (21.81 * 1.17)/(1.13 - 1.17) = -2.58\,\mu\mathrm{g/g}.$$

Calculations of the two above-cited samples have indicated that the lead amount from the dumping is negligible. This result clearly indicates that the dumping has no influence in the lead contamination and proves that the main part of lead contamination is originated from atmosphere.

5 Conclusion

The study of stable and radioactive natural lead isotopes in sediments of the Grand-Maclu and Saint-Point lakes, located 50 km apart, has indicated that the lead pollution is mainly due to an external origin. Lead isotope analysis has confirmed that the lead inputs are principally atmospheric. Lead pollution in the air mainly comes from the industrialized regions of northern France, Germany, Belgium and probably the UK. The lead emissions started with the industrialization of Europe since the end of the 19th century. The Grand-Maclu and Saint-Point lakes show no significant differences in lead concentrations (< 10 ppm) in sediments at around 10 cm depth. These differences are for the most part a function of geographic factors such as exposure to prevailing winds of oceanic origin as well as precipitation of particulate matter. Locally, these variations are controlled by the presence of substantial peaty peri-lacustrine zones or by wetland areas present in each of the catchment areas. The rise in water levels and consequent flooding of these areas during the snow melt period have contributed to the salting-out of metals and therefore of lead which adsorbed onto solid particles. Regular monitoring of lead levels in the waters during March 2008 has confirmed the very low lead concentrations in the water and the lead transfer to the lake by fixing onto solid particles. An enrichment factor value larger than 2 confirms the pollution of the lake sediments with lead. The lead concentration maximum level was reached in the 1970s, followed by a significant reduction in lead inputs, recorded in the Saint-Point lake. Such a behavior of lead was not observed in the sediments of the Grand-Maclu lake. Two distinct periods could be determined in the Grand-Maclu and Saint-Point lakes. The first period ranging from 1920 to 1930 is characterized by a slight increase in the EF values which corresponds to the beginning of the intensive use of lead in gasoline in the USA and Europe. The second period, after the Second World War, is characterized by the resumption of industrialization in the countries of the northern hemisphere.

The isotopic ratios and in particular the $^{206}Pb/^{207}Pb$ ratio, decreasing from 1.22 to 1.14, indicate the progressive increase in lead inputs since the end of the 19th century to the beginning of the 1970s. The subsequent increase of the $^{206}Pb/^{207}Pb$ ratio within the depth fraction between 0 and 7 cm (1970–2005) confirms the decrease of lead inputs and the beginning of the purification of water and its surface sediments.

The similarity of the lead profiles of Grand-Maclu and Saint-Point lakes and the appearance of the first sign of increase in lead concentrations since the end of the 19th century corresponds to results obtained from lead isotope analyses and consequently confirms the external origin of the lead inputs. However, this similarity stops at 5–7 cm depth near the sediment surface of the Grand-Maclu lake. This results from a sedimentation dynamic which is marked by an increase in lead inputs which triggered sub-lacustrine slumping. The undisturbed lead profile in the Saint-Point lake proves that the two locations: the landfill in proximity of this lake and the Pontarlier city, receiving its water, are not responsible for its contamination by the lead.

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References

[1] Agence de l'Eau Rhône Méditerranée et Corse, *Les lacs du Frasnois : Ilay, Narlay, Petit et Grand Maclu. Synthèse de données*, Rapport Interne, Lyon, France, Décembre 2004.

[2] P. G. Appleby, *Radiometric dating of sediment records in European mountain lakes*, J Limnol, 59 (2000), 1–14.

[3] P. G. Appleby, P. J. Nolan, D. W. Gifford, M. J. Godfrey, F. Oldfield, N. J. Anderson, et al., *^{210}Pb dating by low background gamma counting*, Hydrobiologia, 143 (1986), 21–27.

[4] P. G. Appleby and F. Oldfield, *The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment*, Catena, 5 (1978), 1–8.

[5] P. G. Appleby, N. Richardson, and P. J. Nolan, *^{241}Am dating of lake sediments*, Hydrobiologia, 214 (1991), 35–42.

[6] P. G. Appleby, N. Richardson, and P. J. Nolan, *Self-absorption corrections for well-type germanium detectors*, Nucl Instrum Meth B, 71 (1992), 228–233.

[7] S. Ariès, *Mise en évidence de contaminations métalliques historiques à partir de l'étude d'enregistrements sédimentaires de lacs de haute montagne*, PhD thesis, Université Toulouse III – Paul Sabatier, Toulouse, France, 2001.

[8] F. Arnaud, *Signatures climatique et anthropique dans les sédiments holocènes des lacs du Bourget et d'Anterne (nord-ouest des Alpes). Paléohydrologie et contamination au plomb*, PhD thesis, Université des Sciences et Techniques de Lille 1, France, 2003.

[9] F. Arnaud, M. Revel, T. Winiarski, D. Bosch, E. Chapron, M. Desmet, et al., *Lead fall-out isotopic signal over French northern Alps: timing and sources constraints from distant lake sediment records*, J Phys IV, 107 (2003), 61–64.

[10] K. Bell and I. M. Kettles, *Lead-isotope ratio measurements on hummock and hallow peat from Detour Lake area, Ontario*, Geological Survey of Canada, 2003-C3, (2003).

[11] R. Bindler, N. J. Anderson, I. Renberg, and C. Malmquist, *Palaeolimnological investigation of atmospheric pollution in the Søndre Strømfjord region, southern West Greenland: accumulation rates and spatial patterns*, Geology of Greenland survey Bulletin, 189 (2001), 48–53.

[12] J. F. Boyle, *Inorganic geochemical methods in Paleolimnology*, in Tracking Environmental Change Using Lake Sediments. Vol. 2: Physical and Geochemical Methods, W. M. Last et al., eds., Kluwer Academic Publishers, Netherlands, 2001, 83–142.

[13] J. F. Boyle and H. J. B. Birks, *Predicting heavy metal concentrations in the surface sediments of Norwegian headwater lakes from atmospheric deposition: an application of a simple sediment-water partitioning model*, Water, Air, and Soil Pollution, 114 (1999), 27–51.

[14] J. F. Boyle, A. W. Mackay, N. L. Rose, R. J. Flower, and G. Appelby, *Sediment heavy metal record in Lake Baikal: natural and anthropogenic sources*, Journal of Paleolimnology, 20 (1998), 135–150.

[15] J. F. Boyle, N. L. Rose, P. G. Appleby, and H. J. B. Birks, *Recent environmental change and human impact on Svalbard: the lake-sediment geochemical record*, Journal of Paleaolimnology, 31 (2004), 515–530.

[16] J. F. Boyle, N. L. Rose, H. Bennion, H. Yang, and P. G. Appleby, *Environmental impacts in the Jianghan plain: evidence from lake sediments*, Water, Air, and Soil Pollution, 112 (1999), 21–40.

[17] S. J. Brooks, V. Udachin, and B. J. Williamson, *Impact of copper smelting on lakes in the southern Ural Mountains, Russia, inferred from chironomids*, J Paleolimnol, 33 (2005), 229–241.

[18] R. Brugam, I. Bala, B. Vermillon, and W. Retzlaff, *Historical impact of industrial development on groundwater and surface water quality in the American bottoms*, Progress Report, Year 2, Illinois Groundwater Consortium, Southern Illinois University, Edwardsville, July 15, 2002 to July 15, 2003.

[19] A. S. Ek and I. Renberg, *Heavy metal pollution and lake acidity changes by one thousand years of copper mining at Falun, central Sweeden*, Journal of Paleolimnology, 26 (2001), 89–107.

[20] O. Heiri, A. F. Lotter, and G. Lemcke, *Loss of ignition as a matter for estimating organic and carbonate content in sediments: reproducibility and comparability of results*, Journal of Paleolimnology, 25 (2001), 101–110.

[21] J. Hinrichs, O. Dellwig, and H.-J. Brumsack, *Pb in sediments and SPM of the German Bight: natural versus anthropogenic origin*, Applied Geochemistry, 17 (2002), 621–632.

[22] J. Hynynen, A. Palomäki, J. J. Meriläinen, A. Witick, and K. Mäntykoski, *Pollution history and recovery of a boreal lake exposed to a heavy bleached pulping effluent load*, Journal of Paleolimnology, 32 (2004), 351–374.

[23] B. P. Jackson, P. V. Winger, and P. J. Lasier, *Atmospheric lead deposition to Okefenokee Swamp, Georgia, USA*, Environmental Pollution, 130 (2004), 445–451.

[24] C. Kamenik, K. A. Koinig, R. Schmidt, P. G. Appleby, J. A. Dearing, A. Lami, et al., *Eight hundred years of environmental changes in a high Alpine lake (Gossenköllesee, Tyrol) inferred from sediment records*, J Limnol, 59 (2000), 43–52.

[25] M. Krachler, G. Le Roux, B. Kober, and W. Shotyk, *Optimising accuracy and precision of lead isotope measurement (^{206}Pb, ^{207}Pb, ^{208}Pb) in acid digests of peat with ICP-SMS using individual mass discrimination correction*, Journal of Analytical Atomic Spectrometry, 19 (2004), 354–361.

[26] J. E. Landmeyer, P. M. Bradley, and T. D. Bullen, *Stable lead isotopes reveal a natural source of high lead concentrations to gasoline-contaminated groundwater*, Environmental Geology, 45 (2003), 12–22.

[27] R. Nedjai, *Evidence of heavy metal pollution in French Jura lakes: observed impacts and countermeasures*, Information Technologies in Environmental Engineering, Part 10 (2007), 509–524.

[28] R. Nedjai, *A history of lead pollution in nine takes in the Franche-Comté Region, eastern France, through the analysis of lakebed sediments*, International Journal of Water Resources and Environment Management, 1 (2009), 119–133.

[29] S. A. Norton, E. Fjeld, E. Rognerud, and J. L. Jacobson Jr., *Accumulation rates of pollutants and constituents of marine aerosol during the Holocene at Lake Årresjoen, Svalbard, Norway*, in International Conference on Heavy Metals in the Environment, Ann Arbor, MI, August 2000.

[30] I. Renberg, M. W. Persson, and O. Emteryd, *Pre-industrial atmospheric lead contamination detected in Swedish lake sediments*, Nature, 368 (1994), 323–326.

[31] V.-P. Salonen, N. Tuovinen, and S. Valpola, *History of mine drainage impact on Lake Orijärvi algal communities, SW Finland*, Journal of Paleolimnology, 35 (2006), 289–303.

[32] W. Shotyk, M. E. Goodsite, F. Roos-Barraclough, N. Givelet, G. Le Roux, D. Weiss, et al., *Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands*, Geochim Cosmochim Acta, 69 (2005), 1–17.

[33] W. Shotyk, D. Weiss, P. G. Appleby, A. K. Cheburkin, R. Frei, M. Gloor, et al., *History of atmospheric lead deposition since 12,370 ^{14}C yr BP from a peat bog, Jura mountains, Switzerland*, Science, 281 (1998), 1635–1640.

[34] W. Shotyk, D. Weiss, J. D. Kramers, R. Frel, A. K. Cheburkin, M. Gloor, et al., *Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 14C yr BP*, Geochimica et Cosmochimica Acta, 65 (2001), 2337–2360.

[35] D. Tait and B. Thaler, *Atmospheric deposition and lake chemistry trends at a high mountain site in the eastern Alps*, J Limnol, 59 (2000), 61–71.

[36] D. Weiss, W. Shotyk, and O. Kempf, *Archives of atmospheric lead pollution*, Naturswissenschaften, 86 (1999), 262–275.