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(Pre-) historic changes in natural and anthropogenic heavy metals deposition inferred from two contrasting Swiss Alpine lakes

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ABSTRACT

Continuous high-resolution sedimentary record of heavy metals (chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), manganese (Mn), and mercury (Hg)), from lakes Lucerne and Meidsee (Switzerland), provides pollutant deposition history from two contrasting Alpine environments over the last millennia. The distribution of conservative elements (thorium (Th), scandium (Sc) and titanium (Ti)) shows that in absence of human disturbances, the trace element input is primarily controlled by weathering processes (i.e., runoff and erosion). Nonetheless, the enrichment factor (EF) of Pb and Hg (that are measured by independent methods), and the Pb isotopic composition of sediments from the remote lake Meidsee (which are proportionally more enriched in anthropogenic heavy metals), likely detect early mining activities during the Bronze Age. Meanwhile, the deposition of trace elements remains close to the range of natural variations until the strong impact of Roman activities on atmospheric metal emissions. Both sites display simultaneous increases in anthropogenic trace metal deposition during the Greek and Roman Empires (ca 300 BC to AD 400), the Late Middle Ages (ca AD 1400), and the Early Modern Europe (after ca AD 1600). However, the greatest increases in anthropogenic metal pollution are evidenced after the industrial revolution of ca AD 1850, at low and high altitudes. During the twentieth century, industrial releases multiplied by ca 10 times heavy metal fluxes to hydrological systems located on both sides of the Alps. During the last decades, the recent growing contribution of low radiogenic Pb further highlights the contribution of industrial sources with respect to wood and coal burning emissions.

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1. Introduction

The release of toxic heavy metals by human activities to air, soil, and freshwater, is a global problem that threatens living organisms, and strongly challenges the problematic of sustainable development. In this context, natural archives (e.g., lake sediments, peat bogs, and ice cores) are valuable, i) for better understanding the natural sources of trace metals and associated cycling processes by getting information about pre-anthropogenic times, and ii) for reconstructing the impact of past environmental changes and human activities on the temporal and spatial variations of trace metal fluxes. In fact, the lithogenic input of crustal trace elements is highly variable due to natural processes variability, as chemical and physical weathering rates influenced by environmental factors (e.g., climate, soils, lake watershed). That is the reason why ombrotrophic peat bogs are preferentially used as long-term archives of atmospheric metal

deposition, because they are hydrologically isolated from the influence of ground and surface waters, and their inorganic solids are exclusively supplied by atmospheric deposition (Shotyk et al., 1998; Martinez Cortizas et al., 1999). In opposition to bogs and glaciers, lake sediments do not exclusively reflect past atmospheric emissions, but they are more widespread and can thereby provide worthwhile datasets (Eades et al., 2002; Renberg et al., 2002). Moreover, lacustrine sediments generally accumulate continuously and can be precisely dated using radiocarbon techniques as well as natural (e.g., volcanic or flood event) or anthropogenic markers (e.g., artificial radionuclide fallout, fossil fuel combustion residues). As such, sedimentary records offer the possibility to work at high resolution (e.g., seasonal-scale for varved sediment) over the last climatic cycle(s). However, as a prerequisite, the sedimentological processes controlling the natural sediment features need to be understood. For this purpose, the analysis of the sediment density (or porosity) is particularly relevant, because the water content of the sediments i) relies upon the processes of deposition and erosion, and ii) influences the measured weight concentrations. Furthermore, the analysis of a conservative crustal element (e.g., thorium (Th), scandium (Sc), or

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titanium (Ti)) can be used to normalize trace element contents to natural sources, i.e., to discriminate between anthropogenic inputs and natural geological sources.

The most probable source for heavy metal emissions during the industrial period has been mainly identified as coal burning (Shotyk et al., 2003, 2005). Aside from industrial sources, extraction of mercury (Hg) from cinnabar to be used for Hg amalgamation in gold and silver mines has been evidenced to be the main anthropogenic source of Hg for the last 2000 years (Martinez Cortizas et al., 1999; Cooke et al., 2009). It is meaningful to note that the geochemical composition of the heavy metals entrapped in sediment deposits, as produced by either anthropogenic or natural activities, differs according to their geological sources. Despite the recent analytic developments made in the field of Hg isotopes in natural samples (Foucher and Hintelmann, 2006; Gehrke et al., 2009), the current technical development does not allow to discriminate among different Hg sources (Bergquist and Blum, 2009; Kritee et al., 2009). Conversely, the isotopic composition of lead (Pb), which is unaffected by natural fluxes variability and by anthropogenic processes (e.g., smelting), consistently traces the changing sources of pollution (Sturges and Barrie, 1987; Veyseyre et al., 2001). Investigation of long-term continental records notably revealed variations in Pb accumulation and isotopic composition linked to metallurgical activities since the antiquity (Rosman et al., 1997; Cortizas et al., 2002) whereas the largest atmospheric Pb emissions occurred during the 1970s due to the extensive use of leaded gasoline (Moor et al., 1996; Weiss et al., 1999). Although automobile lead emissions subsequently decreased thanks to the policy initiatives concerning the reduction of lead in petrol, other industrial (i.e., Pb smelters, steel-metallurgy plants, waste incineration) or secondary sources (i.e., wood and coal burning) produced a global re-increase in airborne Pb pollution (Chiaradia and Cupelin, 2000; Flament et al., 2002).

The main objective of this study is to evaluate (pre)-historic anthropogenic heavy metals deposition in respect to natural and industrial fluxes, for Central Europe. In this aim, a comparative study has been undertaken on two contrasting environments located on both sides of the Alps: the low-elevation site Lake Lucerne encompasses a large drainage catchment in the Alpine foreland, whereas the high-elevation site Meidsee is a small and remote lake more sensitive to atmospheric inputs. In order to evaluate natural trace element variations, the heavy metal distribution is first compared to intrinsic sedimentological characteristics (density and conservative elements patterns). The paper further highlights the Pb and Hg records, because these two elements with contrasting geochemical behaviours are extremely efficient for deciphering changing rates and sources of pollution in environmental archives (De Vleeschouwer et al., 2010). Moreover, Pb and Hg are measured by independent methods, so that the codistribution of these two elements finally distinguishes human-induced contamination (anthropogenic enrichment of metals) from natural-induced paleoenvironmental changes (natural weathering input of metals).

2. Study sites

2.1. Lake Lucerne

Lake Lucerne (Vierwaldstättersee) is a large lake (surface area: 116 km²) located at an elevation of 434 m a.s.l., at the northern Alpine front in Central Switzerland (Fig. 1). Its maximum depth is 214 m, and the lake encompasses four steep-sided basins separated by moraine ridges which are fed by four alpine rivers (Reuss, Muota, Engelberger Aa and Sarner Aa; Fig. 1) draining a large part of the catchment area of approximately 2250 km². The flow of

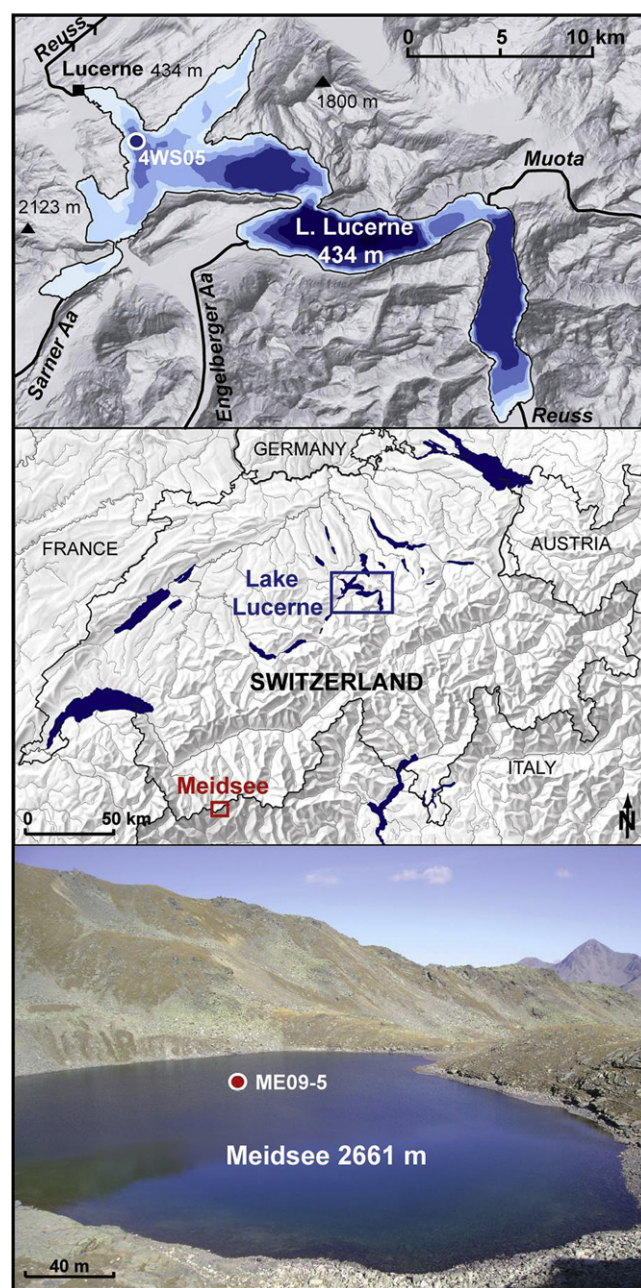


Fig. 1. (Center) Map of Switzerland with the largest Swiss lakes indicated, and the location of the two studied sites. (Top) Topographic and bathymetric map of Lake Lucerne showing the location of the city of Lucerne situated on the outflow River Reuss, and core 4WS05 (bathymetric contour interval is 40 m). (Bottom) Photo of Meidsee showing the location of core ME09-5.

the lake outlet measured in the Reuss at Lucerne between 1922 and 2008 varied from 195 m³/s (minimum value in 1947) to 473 m³/s (maximum value in 2005), with a median value of 283 m³/s (FOEN, 2010). Three basins are relatively isolated from coarse-grained clastic sources, therefore providing suitable sites for studying paleoenvironmental indicators. In 2005, a 163 cm-long gravity core (4WS05, Fig. 1) was collected in the middle of the Chrüztricher Basin (47°03'N, 8°35'E) at 110 m water depth for studying combustion residues (Thevenon and Anselmetti, 2007). The coring was stopped by a turbidite (below 163 cm downcore) related to a major mass-movement event (Schnellmann et al., 2006) (Fig. 2A).

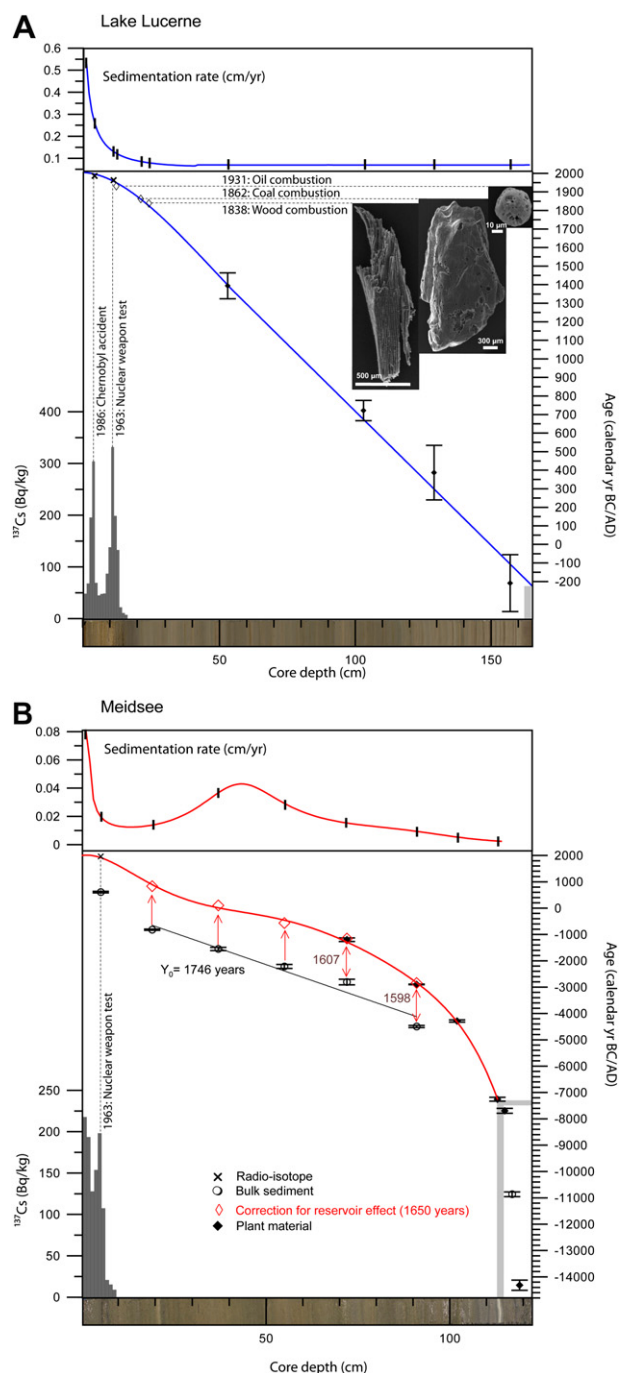


Fig. 2. Sedimentation rates (upper graphs), and age models of the sedimentary sequences from (A) Lake Lucerne, using appearance of combustion products as stratigraphic markers (Thevenon et al., 2010a), the ^{137}Cs peaks (1963 and 1986), and ages in calendar years BC/AD from Table 1; (B) Meidsee, using the ^{137}Cs peak (1963), the ages in calendar years BC/AD of macrorests and bulk sediment samples, after the correction for the reservoir age of the sediment of 1650 years (see details in the text and data in Table 1). Note that the first radiocarbon age (at 5 cm depth, Table 1) was not considered for the age model, because of possible contamination by the atmospheric nuclear weapon tests in 1963.

2.2. Meidsee

Meidsee is a small and remote lake, located at the southern alpine front at an elevation of 2661 m a.s.l. (Fig. 1). The lake has a surface $<1 \text{ km}^2$ with a maximum depth of ca 15 m, and a small catchment area of ca 2 km^2 without any river inflow. In 2009,

a 121 cm-long gravity core (ME09-5) was retrieved from the deepest part of the lake ($46^\circ 13' 25''\text{N}$, $7^\circ 40' 28''\text{E}$). A thin turbidite layer probably due to an erosive event was present at 114 cm downcore (Fig. 2B).

3. Methods

3.1. Bulk density measurement and sampling

Gamma-ray attenuation bulk density was measured on whole-round core with a GEOTEKTM multisensor core-logger. Subsequently, the core was split, photographed and sampled continuously at 1 cm intervals. The sediment samples were frozen, freeze-dried and grounded by hand with an agate mortar.

3.2. ^{137}Cs and ^7Be measurements

Specific ^{137}Cs and ^7Be activities of the recent sediments were determined by gamma spectroscopy using HPGe well detectors (Ortec, GWL series, USA). Efficiency of the detector was obtained by measurement in the same geometry of the soil reference material (IAEA-375). Detection limit is better than 1 Bq/kg.

3.3. Sediment digestion procedure

Around 5–7 mg of sediment powder was mineralized in pure acids in Teflon bombs heated on an electrical hotplate (ca 150°C), in a four-step procedure: 2 ml HNO_3 (suprapur, 65%), a mixture of 1 ml of HClO_4 (suprapur, 70%) with 1 ml HF (suprapur, 40%), and two treatments with 1 ml of HNO_3 (suprapur, 65%). The samples were evaporated between each step of the procedure, and finally diluted to 10 ml with 1% HNO_3 solution for chemical analysis.

3.4. Trace element analysis by inductively coupled plasma mass spectrometry (ICP-MS)

The trace element concentrations (Chromium (Cr), Copper (Cu), Zinc (Zn), Manganese (Mn), Pb, Th, Sc, and Ti), were measured in the digested solution using quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS, Agilent®, model HP 4500). Total variation coefficients of four replicate measurements were smaller than 10%, and the results were expressed in $\mu\text{g/g}$ dry weight sediment.

3.5. Isotopic analysis by thermal ionization mass spectrometry (TIMS)

The Pb isotopic composition was only determined on Meidsee core, because this sequence is less influenced by runoff inputs and covers pre-pollution sediments. Pb was purified by anion exchange chromatography using a AG-MP1-M resin in hydrobromic medium and small volume columns (0.08 ml). Pb was subsequently loaded on Re filaments using the silica gel technique (Gerstenberger and Haase, 1997). All samples (as well as the SRM981 standard) were measured in static mode at a pyrometer-controlled temperature of 1220°C on a multicollector Thermo TRITON mass spectrometer at the Department of Mineralogy of Geneva (Switzerland). Pb isotope ratios were corrected for instrumental fractionation by a factor of 0.1% per amu based on more than 100 measurements of the SRM981 standard and using the standard values of Todt et al. (1996). External reproducibilities (2σ) of the standard ratios are 0.05% for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.08% for $^{207}\text{Pb}/^{204}\text{Pb}$, 0.10% for $^{208}\text{Pb}/^{204}\text{Pb}$, 0.006% for $^{206}\text{Pb}/^{207}\text{Pb}$, 0.007% for $^{208}\text{Pb}/^{207}\text{Pb}$ and 0.008% for $^{208}\text{Pb}/^{206}\text{Pb}$. Total procedural blanks were 120 pg.

3.6. Advanced mercury analysis (AMA)

Total mercury (Hg) was determined by cold vapor atomic absorption spectrometry after thermal decomposition of the sample using an automatic solid analyzer (Altec®, model AMA-254). The detailed procedure is described elsewhere (Cossa et al., 2002). The detection limit (3 SD_{blk}) was $0.005\text{ }\mu\text{g g}^{-1}$ and the reproducibility better than 5%. The method is known as the standard method N 7473 of the US-EPA. The accuracy of the determination for Hg concentrations was estimated using BEST-1 (National research Council Canada); the repeated analyses never exceeded the published concentration ranges ($0.092 \pm 0.009\text{ }\mu\text{g g}^{-1}$).

4. Results

4.1. Chronostratigraphy

4.1.1. Lake Lucerne age model

A former age model of core 4WS05 has been published in Thevenon and Anselmetti (2007) using the morphology of the fly-ash particles emitted by the steamboats, which successively burned wood (AD 1838), coal (AD 1862), and oil (AD 1931). These results are in agreement with ages determined in the present study using the radiocesium (^{137}Cs) activity (Fig. 2A). Two distinct ^{137}Cs peaks were present in core 4WS05, attributed to the Chernobyl accident in AD 1986 and to the maximum radionuclide fallout from atmospheric nuclear tests in AD 1963/64 (at 4 and 11 cm, respectively; Fig. 2A). The age model for the lower part of the core was constrained using two radiocarbon dates published in Thevenon and Anselmetti (2007), and two new radiocarbon dates (ETH-37378 and ETH-37379) also carried out on leaves remains (Table 1). The radiocarbon date obtained at 157 cm downcore (ca 208 BC) confirmed that the turbidite observed at 163–166 cm depth is related to the large pre-historic earthquake that occurred in Central Switzerland ca 2200 years ago (Strasser et al., 2006) (Fig. 2A).

4.1.2. Meidsee age model

The presence of beryllium (^7Be) within the first cm of the core is evidence for recent sedimentation, and the depth profile of ^{137}Cs shows a peak attributed to the AD 1963 maximum ^{137}Cs emissions from aerial nuclear weapon tests at 5 cm depth in the core (Fig. 2A).

Six radiocarbon dates were performed on plant material (leaves and wood remains, Table 1), while six radiocarbon dates on bulk sediment samples provided apparent older ages (Fig. 2A). The age differences obtained on different materials from the same depth (1607 years at 72 cm, and 1598 years at 91 cm) and the intercept of the linear regression line (1746 years) are used to estimate the reservoir age of the sediment: ca 1650 years (Standard Deviation = 83, $n = 3$; Fig. 2A) (Hedenström and Possnert, 2001; Doner, 2003). Such an old carbon effect might originate from the input of stable and old refractory organic matter present in Alpine podzols (Favilli et al., 2009; Egli et al., 2009). A relatively old ^{14}C date of macrorests was found for the beginning of the record (ca 14315 BC at 119 cm), confirming the age of the earliest formation of Pleistocene/Holocene-age Alpine soils (Favilli et al., 2008). Although there is no evidence for any discontinuity in the sedimentary record, some interruption in sedimentation (or lag time) may have occurred during subsequent cold climate reversals (e.g., Younger Dryas ca 12000 years ago; Muscheler et al., 2008). For this reason, the depth-age curve was only generated down to the turbidite deposited at 114 cm (ca 7500 BC, Fig. 2A).

4.2. The distribution of trace elements

The concentrations of trace elements are first plotted against depth for Lake Lucerne (Fig. 3A) and Meidsee (Fig. 3B). Before the industrial revolution, the trace metal (Cr, Cu, Zn, Mn, Pb, and Hg) distribution shows a similar pattern of variation to that observed for Th, Sc and Ti profiles, indicating a homogeneous source sustained by natural weathering inputs. In order to get rid of this sedimentological signal, Pb, Cu, and Hg have been normalized to the conservative crustal element Sc and expressed in the form of enrichment factors (EF_s), respectively calculated as the ratio of Pb/Sc, Cu/Sc, and Hg/Sc in the sediment samples, and normalized to concentrations in the earth's Upper Continental Crust (UCC) (Wedepohl, 1995). For instance, the mean ratios of Pb/Sc in Meidsee sediments before 5000 BC, and in Lake Lucerne sediments before JC, are 7.6 ($n = 16$) and 4.3 ($n = 14$), respectively. For comparison, the pre-anthropogenic Pb/Sc ratio of atmospheric soil dust from a Swiss peat bog is 4.0 (Shotyk et al., 2002). By the same way, the Hg/Sc ratio of 0.005 from Lucerne (before JC) is almost similar to the one of 0.006 from Meidsee (before 5000 BC). The

Table 1

Lake Lucerne (upper part) and Meidsee (lower part) AMS ^{14}C ages, in conventional radiocarbon years BP (before present = 1950) carried out at the AMS ^{14}C laboratory at the ETH/PSI AMS facility in Zurich (Switzerland); calibrated ages in calendar years (BC/AD) using Oxcal v4.0 calibration program (1σ , 68.2% probability) with the terrestrial calibration curve IntCal04 (Bronk Ramsey, 2001)

Depth (cm)	Type of material	Sample number	AMS ^{14}C age BP 1950 (year)	Age before AD 2010 (year)	Calendar age BC/AD (year)	$\delta^{13}\text{C}$ (‰)
53	Leaves	ETH-31562	490 \pm 65	616 \pm 70	1394 \pm 70 AD	−21.9 \pm 1.2
103	Leaves	ETH-31563	1280 \pm 55	1288 \pm 54	721 \pm 54 AD	−25.9 \pm 1.2
129	Leaves	ETH-37378	1675 \pm 120	1623 \pm 147	387 \pm 147 AD	−31.3 \pm 0.5
157	Leaves	ETH-37379	2155 \pm 125	2218 \pm 153	208 \pm 153 BC	−29.0 \pm 0.5
5	TOM	ETH-39651	1460 \pm 35	1402 \pm 31	AD 608	−19.0 \pm 1.1
19	TOM	ETH-38960	2660 \pm 35	2830 \pm 25	AD 830 ^a	−17.2 \pm 1.1
37	TOM	ETH-38961	3265 \pm 35	3560 \pm 60	AD 100 ^a	−24.8 \pm 1.1
55	TOM	ETH-38962	3790 \pm 35	4225 \pm 75	565 ^a BC	−24.3 \pm 1.1
72	TOM	ETH-39513	4230 \pm 50	4815 \pm 105	1155 ^a BC	−22.9 \pm 1.1
72	Wood	ETH-38717	2980 \pm 30	3208 \pm 68	1197 BC	−32.9 \pm 1.1
91	Leaves	ETH-38846	4275 \pm 30	4907 \pm 12	2897 BC	−28.1 \pm 1.1
91	TOM	ETH-39652	5655 \pm 40	6505 \pm 41	2845 ^a BC	−19.8 \pm 1.1
102	Leaves	ETH-38847	5405 \pm 30	6296 \pm 41	4286 BC	−27.9 \pm 1.1
113	Wood	ETH-38718	8240 \pm 35	9265 \pm 71	7256 BC	−33.2 \pm 1.1
115	Leaves	ETH-38963	8715 \pm 45	9705 \pm 95	7695 BC	−28.9 \pm 1.1
117	TOM	ETH-39653	10960 \pm 45	12875 \pm 90	10865 BC	−14.9 \pm 1.1
119	Leaves	ETH-38719	13670 \pm 50	16325 \pm 195	14315 BC	−30.9 \pm 1.1

^a The bulk sediment samples dates are corrected for a reservoir age of 1650 years (see details in the text and in Fig. 1).

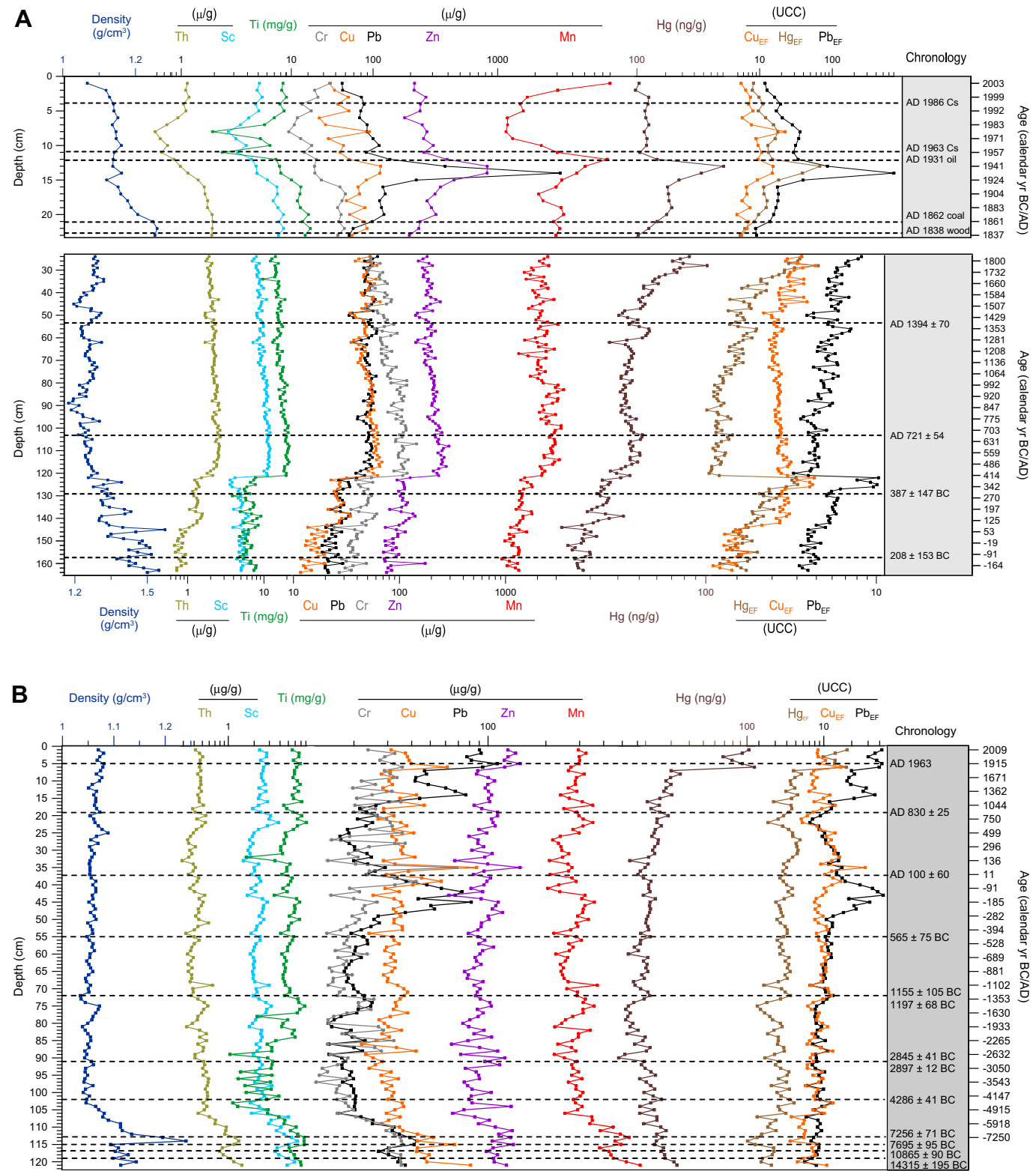


Fig. 3. Density, Th, Sc, Ti, Cr, Cu, Pb, Zn, Mn, Hg, Hg_{EF}, Cu_{EF}, Pb_{EF} of Lake Lucerne (A) and Meidsee (B) as a function of depth (cm, left axis), with the corresponding age (calendar yr BC/AD) on the right axes. The radiocarbon dates (calendar yr BC/AD from Table 1) are reported on the right side.

calculated lithogenic backgrounds for Pb and Hg are eventually normalized to the UCC lithogenic ratios of 0.93 and 0.0025, respectively, and reported on Fig. 4. In Lake Lucerne, the abrupt rise in trace elements contents together with the decrease in the

density profile around 122 cm (ca AD 400) likely indicates important changes in sediment composition and texture due to increased chemical weathering and runoff, rather than anthropogenic emissions. In response to this natural increase in lithogenic

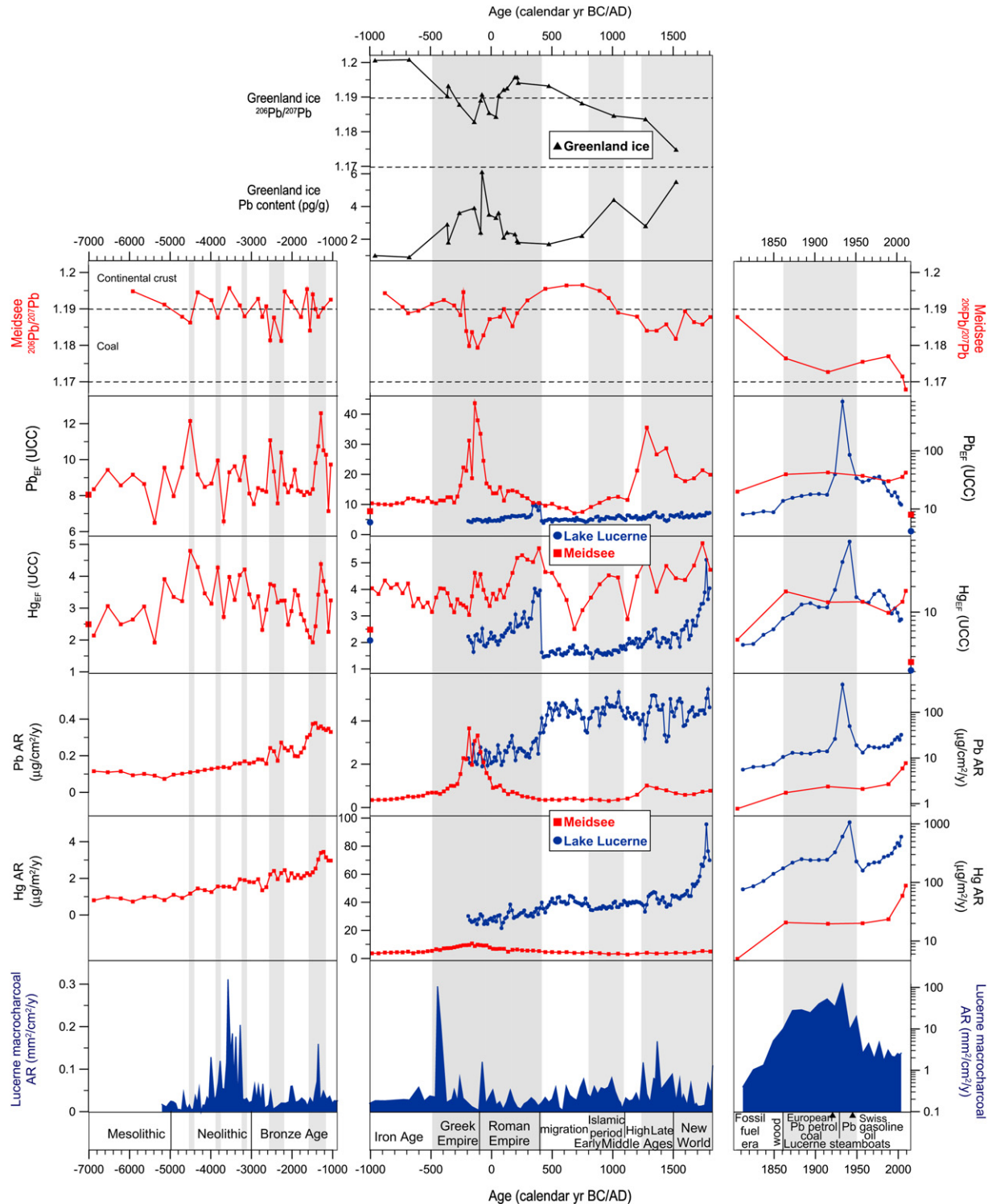


Fig. 4. Meidsee $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, and Pb_{EF}, Hg_{EF}, Pb AR, Hg AR, of Lake Lucerne and Meidsee as a function of age (calendar yr BC/AD), compared with Greenland ice Pb record (Rosman et al., 1997), Lake Lucerne macrocharcoal AR (Thevenon and Anselmetti, 2007), and the cultural chronology on the lower part. The local Pb and Hg lithogenic backgrounds relative to UCC values are reported on EF vertical axes (details in the text).

inputs, EF_s values abruptly dropped (Fig. 3A and Fig. 4). Concerning the Meidsee sequence (Fig. 3B), the enriched trace elements concentrations combined to higher density values downcore (below 105 cm; ca 5000 BC) indicate coarser sediment features enhanced by physical weathering and erosion, associated with the lake formation during the early deglaciation rather than human or

volcanic sources. In contrast, the strong upcore enrichments in trace metals, which do not covary with sedimentological tracers (e.g., density, and Sc), certainly indicate enhancement of anthropogenic sources (Fig. 3A and B).

In order to compare the two records by taking into account the differences in deposition rate, the concentrations of Pb and Hg have

been converted to Accumulation Rates (AR) by using the following equation:

$$\text{PbAR}(\mu\text{g}/\text{cm}^2/\text{yr}) = \frac{\text{concentration} \times \text{sedimentation rate} \times \text{density}}{\text{rate} \times \text{density}} \quad (1)$$

$$\text{HgAR}(\mu\text{g}/\text{m}^2/\text{yr}) = \frac{10 \times \text{concentration} \times \text{sedimentation rate} \times \text{density}}{\text{rate} \times \text{density}} \quad (2)$$

with the concentration of Pb in $\mu\text{g}/\text{g}$ and Hg in ng/g , sedimentation rate in cm/yr , and sediment bulk density in g/cm^3 .

Pb and Hg concentrations are slightly higher in Lake Lucerne sediments (ca 27 ng/mg for Hg and 22 $\mu\text{g}/\text{mg}$ for Pb) as compared to Meidsee (ca 17 ng/mg for Hg and 19 $\mu\text{g}/\text{mg}$ for Pb) (Fig. 3A and B). However, the trace element flux is more than 5 times higher in Lake Lucerne than in Meidsee, due to higher runoff inputs and sedimentation rate (ca 0.07 cm/year for Lake Lucerne and ca 0.02 cm/year for Meidsee) (Figs. 2 and 4). The Meidsee pre-historic record allows an estimation of the range of natural background fluxes to be around 0.1–0.4 $\mu\text{g}/\text{cm}^2/\text{y}$ for Pb and 1–4 $\mu\text{g}/\text{m}^2/\text{y}$ for Hg (Fig. 4). These values are consistent with pre-anthropogenic atmospheric Hg fluxes in the Arctic and temperate zone, which were also 10–20 times lower than recent deposition rates (Shotyk et al., 2003; Givelet et al., 2004).

5. Discussion

5.1. Deposition history of pollutants

During the Neolithic (e.g., 3800 BC) and the Bronze Ages (e.g., 2500 BC), peculiar Pb isotopic values (Figs. 4 and 5) associated with slight enrichment in metals (e.g., Cu, Pb, and Hg; Figs. 3 and 4) could suggest a local- to regional-scale pollution impact linked to the earliest phase of agriculture in Central Europe and early metallurgy, respectively (Shotyk et al., 1998; Kalis et al., 2003; Turney and Brown, 2007). This assumption might be supported by the charcoal record from Lake Lucerne (Fig. 4), showing concomitant increases in fire activity due to major anthropogenic changes (lake dwellings, land-use changes, technological innovations; Thevenon and Anselmetti, 2007). One must note however that EF_s remain relatively low during pre-historic times, so that sedimentological variations primarily influence trace element inputs (Fig. 3B and Fig. 4). Such finding is also supported by the very slight and constant increase of Pb and Hg fluxes from 5000 to 1000 BC, which are not paralleled by the EF_s curves but resulted from the steady increase of the sedimentation rate (Fig. 2B and Fig. 4). By contrast, the Meidsee record exhibits Pb fluxes more than two times higher than background levels around 300 BC, i.e., during the Greek Empire. During the following Roman Empire, atmospheric Pb emissions abruptly rise, as attested by the great anthropogenic Pb deposition between ca 300 BC and AD 100 and the growing importance of non-radiogenic Pb (Fig. 4). The strong similarity of the Meidsee Pb profiles with those from the Greenland ice core is remarkable (Fig. 4), deciphering i) the early large-scale atmospheric pollution by the Roman civilization, ii) the capacity of Meidsee to provide large-scale atmospheric pollution record, and iii) the Spanish mining region as a potential source for the atmospheric lead deposited at high altitude in the Southern Alps (Rosman et al., 1997). In fact, Hg has been mined for ca 2000 years in the Almadén district (central Spain), where Spanish mines alone have contributed to one third of the total historic production of Hg (Hylander and Meili, 2003). In addition, a peat bog record from northwest Spain showed roughly synchronous increasing anthropogenic Pb and Hg releases from

Iberian ores by ancient mining, when cinnabar refining process was introduced (Nriagu, 1983; Domergue, 1990; Martinez Cortizas et al., 1999, 2002).

In Meidsee, the heavy metal fluxes continuously decrease following the decline of the Roman Empire (ca AD 400), and remain low during the subsequent cold Migration period (ca AD 375–534), which is known as a period of land abandonment and reforestation in Northwest Europe (Berglund, 2003). Afterwards, anthropogenic pollutants significantly rise during the Spanish-Islamic Golden Age (ca AD 800–1100), and especially during the Late Middle Ages (ca AD 1400). Synchronous lower radiogenic Pb deposition and higher biomass burning activity around Lake Lucerne (Fig. 4) also point to increases in anthropogenic sources of pollutants. Meanwhile, a short and abrupt decline in anthropogenic trace metal deposition occurs around AD 1300 (Fig. 4). This latter period is characterized by the Great Famine (AD 1315–1321) and one of the deadliest pandemics in human history (Black Plague), peaking in Europe between AD 1346 and 1353 (Hays, 2005). Interestingly, Hg_{EF} and Hg flux strikingly increase in Lake Lucerne after AD 1550, while Pb_{EF} and Pb flux remain fairly constants (Fig. 4). Such a relative decrease in anthropogenic Pb deposition and biomass burning activity compared to increasing anthropogenic Hg, could be linked to historical changes in ore extraction. Indeed, European Pb mining and consumption of firewood declined after ca AD 1550 as the exploitation of metal resources in Americas increased (Nef, 1987; Burt, 1995; Brännvall et al., 2001). In fact, the use of Hg to amalgamate and concentrate precious metals (i.e., gold and silver) increased after the development of the “Patio” amalgamation process by Bartolomeu de Medina in 1554, reaching its apogee around AD 1880 (Nriagu, 1994; Lacerda, 1997). The resulting increase in Hg emissions from cinnabar ores smelting and burning of amalgams might have strongly increase global atmospheric depositions of Hg, as reported by several authors in areas far from these mining locations (Martinez Cortizas et al., 1999; Givelet et al., 2003). Finally, this time period also coincides with a major change in the isotope composition of the carbonaceous aerosols ($\delta^{13}\text{C}_{\text{black carbon}}$) deposited at Colle Gnifetti glacier (Swiss–Italian Alps, 4455 m a.s.l.; Thevenon et al., 2009).

After the Industrial Revolution of ca AD 1850, great accumulation of combustion residues in Lake Lucerne parallels Pb and Hg increases, identifying steamboat traffic as a major pollutant source (Fig. 4; Thevenon and Anselmetti, 2007). Lake Lucerne anthropogenic Pb and Hg fluxes exceed by more than 100 times the natural inputs around AD 1920, due to the local abundance of fossil fuel combustion residues emitted by the steamboats (Thevenon and Anselmetti, 2007) (Fig. 3A and Fig. 4). Although pollutant emissions stop to increase afterward, Pb and Hg fluxes to Lucerne and Meidsee re-increase during the last decades, remaining more than 10 times higher than natural background levels. Samples collected from the main water inflows and river sediments during summer 2009 identify the Reuss River (Fig. 1) as the only riverine input of pollution to Lake Lucerne ($\text{Pb}_{\text{EF}} \sim 15$ for sediment and water samples).

5.2. Isotopic composition of Pb

Natural Pb background isotopic composition can be estimated from Meidsee record using the pre-Neolithic sediments characteristics (Fig. 5B). Such level is almost reached during periods of reduced anthropogenic emissions (e.g., ca AD 400–800), while the growing contribution of non-radiogenic Pb releases is associated with rises in anthropogenic Hg and Pb deposition (Fig. 4). Fig. 5A plots the Pb_{EF} and Hg_{EF} against the $^{208}\text{Pb}/^{207}\text{Pb}$ values to illustrate i) changes in the Pb isotopic composition with increasing anthropogenic aerosols deposition, and ii) Pb_{EF} and Hg_{EF}

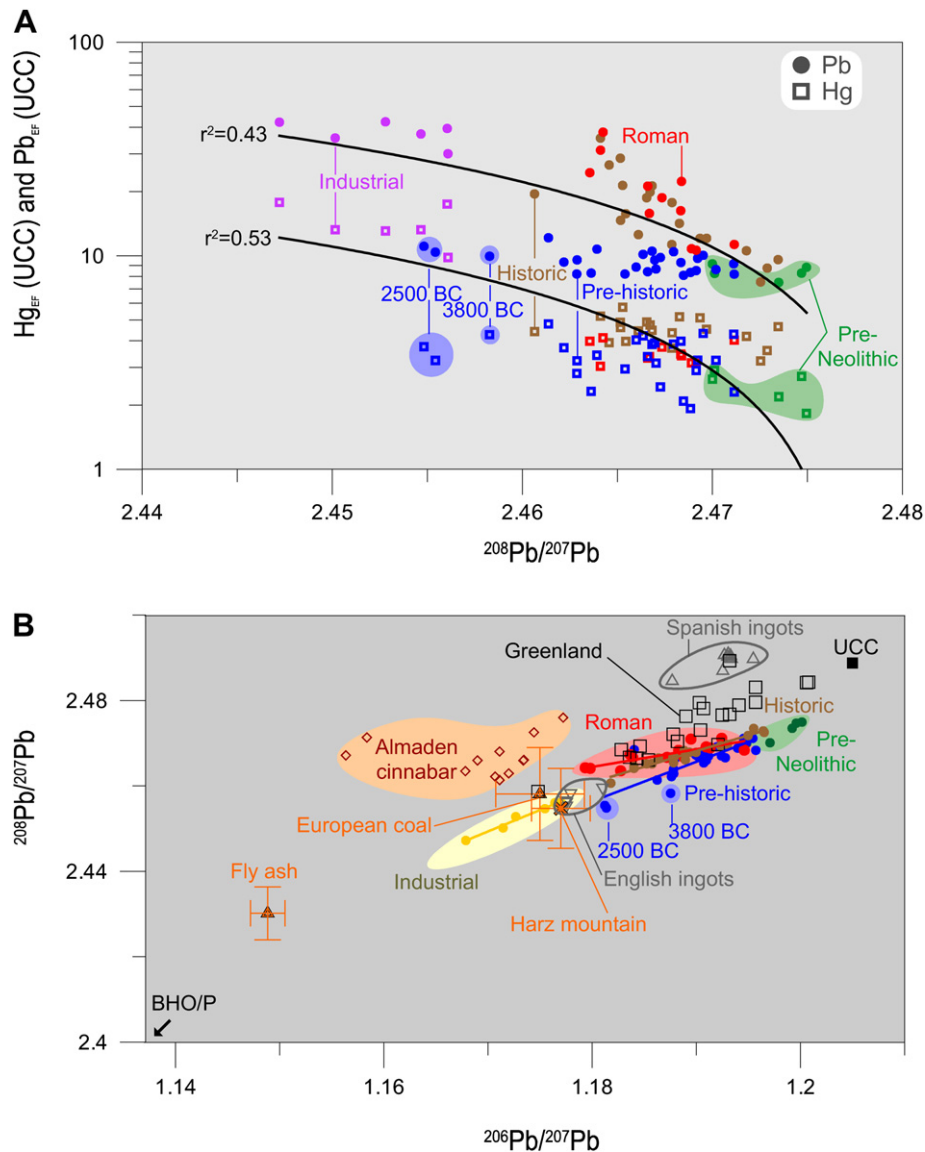


Fig. 5. Meidsee isotope systematics: (A) Pb_{EF} (circles) and Hg_{EF} (squares) as a function of $^{208}Pb/^{207}Pb$ ratios. (B) $^{208}Pb/^{207}Pb$ ratios as a function of $^{206}Pb/^{207}Pb$ ratios. The Pb isotope signatures for Greenland ice core (Rosman et al., 1997), European coal fuel combustion and incinerator fly ash (data source: Kylander et al., 2005), archeological artifacts (Spanish and English ingots; Labonne et al., 1998), and cinnabar for Almaden district (Higueras et al., 2005) are reported for comparison. Errors bars have been multiplied by 0.2. The isotope signatures of the Broken Hill Mine Ore (BHO) and leaded petrol (P) plot off the graph. The Meidsee record is divided into five chronostratigraphic units: The pre-Neolithic (<6000 BC), pre-historic (5500–700), the Greek and Roman (600 BC–AD 100), historic (AD 100–1800), and post-industrial (>AD 1850) periods.

correlations ($P < 0.001$, $n = 71$) with Pb isotopic compositions ($r^2 = 0.43$ and 0.53 , respectively). On Fig. 5B, the Meidsee Pb isotopic compositions are compared with potential lead sources: cinnabar from the Almaden district (Higueras et al., 2005), Spanish and English ingots representative of Pb extracted from those local ores during the first and second century, respectively (Labonne et al., 1998), Pb derived from the Harz Mountain ore bodies (Germany; Monna et al., 2000), and incinerator fly ash and European coal (data from Kylander et al., 2005). The Pb isotope systematics of Meidsee is therein separated into five chronostratigraphic units (Fig. 5B). The first unit (<6000 BC) includes the pre-Neolithic sediments (characterized by the highest isotopic ratios), and identifies the regional background (pre-pollution) end-member. The second unit (5500–700 BC) shows the deposition of less radiogenic Pb (that may have an anthropogenic component), which probably indicates the early development of pre-historic metallurgy in Europe, for example mining and

smelting activities from the Harz Mountain (Monna et al., 2000). The following historic samples (AD 100–1800) present a roughly similar slope, with mixing values between local lithogenic background and ore smelting (e.g., English ingots), or coal burning (e.g., European coal). The polluted Greek and Roman samples (600 BC–AD 100), which recorded the highest pre-industrial anthropogenic Pb deposition, display a trend with a slightly different slope, consistent with higher contributions from Pb ore sources (e.g., Almaden cinnabar). This last result strikingly agrees with those of the Greenland ice record (Figs. 4 and 5B), whose isotopic systematics point to the mining districts in south Spain as the dominant Pb sources during the Roman Empire (Rosman et al., 1997). Although the signature of the Spanish ingots (from the Cartagena area) shows consistency with the Pb isotope data from the Greenland aerosols, this source ranges off the main mixing lines of Meidsee (Fig. 5B). Finally, the Pb isotope ratios for the industrial period (>AD 1850) are much more depleted in

radiogenic Pb, due to massive fossil fuel combustion emissions, for instance petroleum and power plant incinerator (fly ash) sources. It is known that in Switzerland, atmospheric Pb isotopic composition shifted after AD 1960, due to the introduction of leaded gasoline in AD 1947 (Nriagu, 1990; Shotyky et al., 2002). Although lead emission by automobile traffic has decreased largely during the last decades, other industrial sources (e.g., coal combustion, smelting, or waste incinerators) have relatively increased, as reflected by less radiogenic Pb deposition in Meidsee and increasing heavy metals fluxes in both lakes. Such findings therefore highlight the increased relative contribution of industrial releases since AD 1960, while automobile was no longer the major atmospheric source of heavy metals in European countries (Flament et al., 2002).

6. Conclusions

During the pre-historic period, trace metal deposition is primarily controlled by the sedimentological response to natural environmental changes (physical and chemical weathering processes). Although Neolithic deforestation and early metallurgy possibly enhanced trace elements emissions, EF_s remain fairly low and Pb and Hg fluxes did not over-exceed sedimentological variations before Roman mining activities. As a matter of fact, great increase in Pb depositions successively highlight the impact of the extensive mining industry during the Greek and Roman periods (from ca 300 BC to AD 400), the Late Middle Ages (ca AD 1400), the Early Modern Europe (after ca 1600), and the Industrial Revolution (after ca 1850). Pre-industrial anthropogenic Pb deposition at high altitude in the Southern Alps strongly resembles that deposited onto the Greenland ice sheet, pointing to the homogeneous pollution of the Northern hemisphere sustained by long-range transport of air pollutants from mid-latitude regions (Hong et al., 1994). Such results are in agreement with the intercontinental transport of Saharan mineral dust that occasionally reaches Summit Greenland (Thevenon et al., 2010b). Meidsee Pb isotopic composition furthermore evidences the European contribution and the impact of extensive fossil fuel combustion. Moreover, Pb atmospheric emissions did not drop following the decline of Pb gasoline additives in Europe, pointing to the increasing relative contribution of industrial sources. Overall, Pb_{EF} and Hg_{EF} exhibit roughly similar patterns of variation controlled by human practices (e.g., mining, metallurgy), suggesting large-scale contamination and/or a synchronicity in societal changes. However, discrepancies in Pb and Hg profiles during Early Modern Europe (after ca AD 1550), suggest a change in sources of Hg atmospheric pollution linked to gold and silver mining innovation (i.e., Hg amalgamation process, coal burning). Such results finally insist on the importance of understanding natural metal flux variability with regard to weathering response, and the interest of combining multi-trace elements and Pb isotopic analyses for reconstructing natural and human-induced environmental changes.

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