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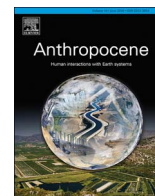
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Research paper

Atmospheric and terrigenous metal accumulation over 3000 years in a French mountain catchment: Local vs distal influences



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ABSTRACT

In this paper we report analyses of four peat cores taken from a mountain valley in the French Pyrenees where ancient metallurgical and agro-pastoral activities have occurred. By combining a range of geochemical and chronological proxies we investigated (1) the importance of PHTE (Potentially Harmful Trace Element) accumulation during pre-industrial times compared to recent accumulation, and (2) the intimate relationship between landscape use and terrestrial PHTE transfers. We show how long human-environment interaction in mountain environments and pre-industrial anthropogenic activities led to PHTE accumulation equal to or even exceeding that of modern times. Atmospheric contamination by PHTE occurred throughout 500 BC – AD 500 for lead (Pb) and antimony (Sb), AD 1200–1600 for only Pb, and the last 150 years for Pb, Sb and copper (Cu) combined. Lead isotopes allowed determination of the impact of Pb contamination from significant local mining and metallurgical activities during the Middle Ages. An estimation of PHTE inventories derived from atmospheric deposition suggests that 85% of Pb accumulation occurred before AD 1800, thus highlighting the influence of past local activities to the accumulation of atmospheric contaminants compared to that of more recent periods. Enhanced erosion input to one of the mires is evident from AD 1600 to 1950, and intensive grazing coupled with forest clearings are the likely cause of these rapid transfers of natural PHTE and previously stored Pb to downstream mires. Remobilized Pb in the impacted peatland represent at least one third of the total Pb-inventory, suggesting that terrestrial transfers were important and acting as hotspot sources of PHTE accumulation.

1. Introduction

Anthropogenic fluxes of up to 62 chemical elements surpass their corresponding natural fluxes (Sen and Peucker-Ehrenbrink, 2012). Among those elements some metals and metalloids, such as lead (Pb) or antimony (Sb), are considered as potentially harmful trace elements (PHTE; Plant et al., 1997) with limited or no biological function. Previous studies have clearly shown that widespread PHTE contamination of especially Pb, as recorded in ice cores (Hong et al., 1994; Rosman et al., 1997; Zheng et al., 2007), peat cores (Shotyk et al., 1998; Martinez Cortizas et al., 2002) and in lake sediments (Renberg et al., 1994; Camarero et al., 1998), occurred from the onset of metallurgical processing leaving a millennial scale pollution history.

Due to their geological features, e.g. ore deposits, mountain environments have been exploited since the beginning of the practice of metallurgy. Pre-

industrial contamination of Pb has been evidenced in several European mountain ranges (De Vleeschouwer et al., 2014 and references therein) and European medieval mining and metallurgy is considered to be the cradle of the industrial contamination by PHTE in general, and Pb in particular (Brännvall et al., 1999). Based on our review of available literature and our own unpublished data, European mountain soils stored at least 800 mg m² of locally derived Pb before the Industrial Revolution (i.e. prior to 1800; see Table 1 and Table S1 in Supplementary information – SI), sometimes equal to or exceeding industrial contamination. Yet, even though PHTE are known to be concentrated in mountain soils, the legacy of trace metal stocks in mountain zones, in relation to environmental changes, is still poorly understood (Le Roux et al., 2010; Stankwitz et al., 2012).

The Pyrenees are no exception to this pre-industrial contamination as many mining and metallurgical sites were present in the region, of which some are dated as far back as the Bronze Age (Monna et al.,

Abbreviations: PHTE, potentially harmful trace element; EF, enrichment factor; AR, accumulation rate; ESLP, European Standard Lead Pollution

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Table 1
Total inventories and calculated anthropogenic inventories of PHTE (Pb, Cu, Sb) in the EM, Escale, RN3 and W1652A cores of Bassiès Valley, Black Forest Mountain, Germany; Le Roux et al., 2005) and EGR (Jura Mountain, Switzerland; Shoty et al., 1996 + 1998) inventories have been included for comparison.

Period	400 BC–500 AD		500 AD–1000 AD		1000 AD–1200 AD		1200 AD–1600 AD		1600 AD–1800 AD		1800 AD–1950 AD		1950 AD–Present		Total	
Pb Inv. (mg m^{-2})	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}
EM	1157	1001	437	335	143	99	1416	1190	1285	1005	1522	1205	330	291	6290	5126
Escale					115	80	1077	930	223	186	254	231	244	217	1913	1644
RN3															485	419
W1652A															405	382
Black Forest	650		190		260		920		210		1330				3560	
EGR	200		60		40		250		180		1730				2460	
Cu Inv. (mg m^{-2})	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}
EM	119	34	61	9	28	5	123	8	128	0	170	0	52	31	681	87
Escale					33	15	99	19	26	5	17	5	45	31	220	75
RN3															83	73
W1652A															77	62
Sb Inv. ($\mu\text{g m}^{-2}$)	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}	Inv	Inv _{Ant}
EM	8.5	6.5	2.4	1.2	0.7	0.1	4.8	0.7	5.6	1.0	9.8	4.7	3.5	3.0	35.3	17.3
Escale					0.7	0.3	2.4	0.7	0.5	0.1	2.7	2.5	3.6	3.4	9.9	7.0
RN3															2.3	2.0
W1652A															5.8	5.4
Black Forest	5.7		1.3		1.4		6.4		3.6		28				47	
EGR	2.9		0.4		0.5		2		2.3		28				36	

Inv = Total inventory, Inv_{Ant} = Anthropogenic inventory Estimated with PHTE/L.

2004a; Galop et al., 2013). Bassiès valley is located in the Vicdessos region within the Pyrenees Mountain Range (Ariège, FRANCE). Ancient human activities *i.e.* forest clearings, charcoal production and cattle grazing, have been ongoing since the late Neolithic (Galop and Jalut, 1994; Galop, 1998) and were intensified during the Middle Ages in order to supply charcoal for metallurgical activities. On the western side of the valley (Aulus-les-Bains mining district) copper- (Cu), silver- (Ag) and Pb-ores were exploited, while iron (Fe) ores were extracted and smelted on the eastern side (Dubois, 1999). The processing and smelting of ores could potentially have caused local atmospheric contamination of PHTE (Bindler et al., 2011; Karlsson et al., 2015). Further to this, in the Bassiès catchment, erosion has been closely related to cattle grazing, *i.e.* with the abandonment of intensive pastoral activities in the 1960s a clear decrease in erosion rates have been shown (Galop et al., 2011).

Remobilization of contaminants stored in mountain organic soils can influence contaminant loads in fluvial systems and downstream mountain lakes (Kaste et al., 2003). Watershed inventories of PHTE have shown that Pb related to industries and leaded gasoline, and Pb stored in Pyrenean soils, was remobilized and transferred to downstream lakes several years after the contamination occurred (Bacardit and Camarero, 2010). The quality of lake sediments and water could therefore be impacted by remobilized PHTE which could also be further transferred into the aquatic food chains. For example, it has been shown that contamination of Pb has reached aquatic mosses (Camizuli et al., 2014) and even high trophic level organisms such as trout in or near mining environments (Monna et al., 2011; Paris et al., 2015).

Geochemical records of contamination from peatlands often are used to estimate the deposition of PHTE (*i.e.* atmospherically derived contamination only when the peatlands are ombrotrophic; Hansson et al., 2015 and references therein). Since elements associated with soil dust (Ti, Rare Earth Elements – REE), including PHTE (Pb, Sb, Cu), are relatively retained within the peat column, peat chemical profiles provide valuable records of PHTE accumulation and enable reconstruction of pollution history.

In this study, we investigated PHTE accumulation over time in four peat profiles from a small mountain valley in the Pyrenees that has undergone more than 2000 years of human activities. The objective was to show the long human-environment interaction in mountain environments and the influence that pre-industrial anthropogenic activities have had on PHTE accumulation. Specifically, we studied: 1) The importance of PHTE accumulation during preindustrial times compared to recent PHTE deposition, and 2) The close relationship between past human activities and the remobilization of terrestrial PHTE within this high mountain catchment. We show that the impact of pre-industrial to recent human activities in European mountains could be equal to those of the Neolithic or the Bronze Age-Antiquity-era. Further, and more importantly, we show that these recent human activities were not necessarily restricted to merely the last 50 to 200 years but rather extending over centennial scales.

2. Methods

2.1. Sampling and handling

We selected four peat bogs and mires, *i.e.* minerotrophic peatlands with ombrotrophic near surface characteristics in the form of *Sphagnum* hummocks, in the Bassiès valley. All sites were at close proximity to each other to guarantee a representative spatial coverage over the watershed (Fig. 1). Our own geological survey and French Geological Survey missions showed that, contrary to the western opposite slope, there is no ore mineralization in this valley. RN3 is a blanket bog located on a plateau, isolated from lateral water and mineral input. Escale and W1652 are located over flat areas. The last mire, called Etang Mort (EM), is located in a small catchment within the valley and represents more than 3000 years of continuous peat accumulation. The age of the

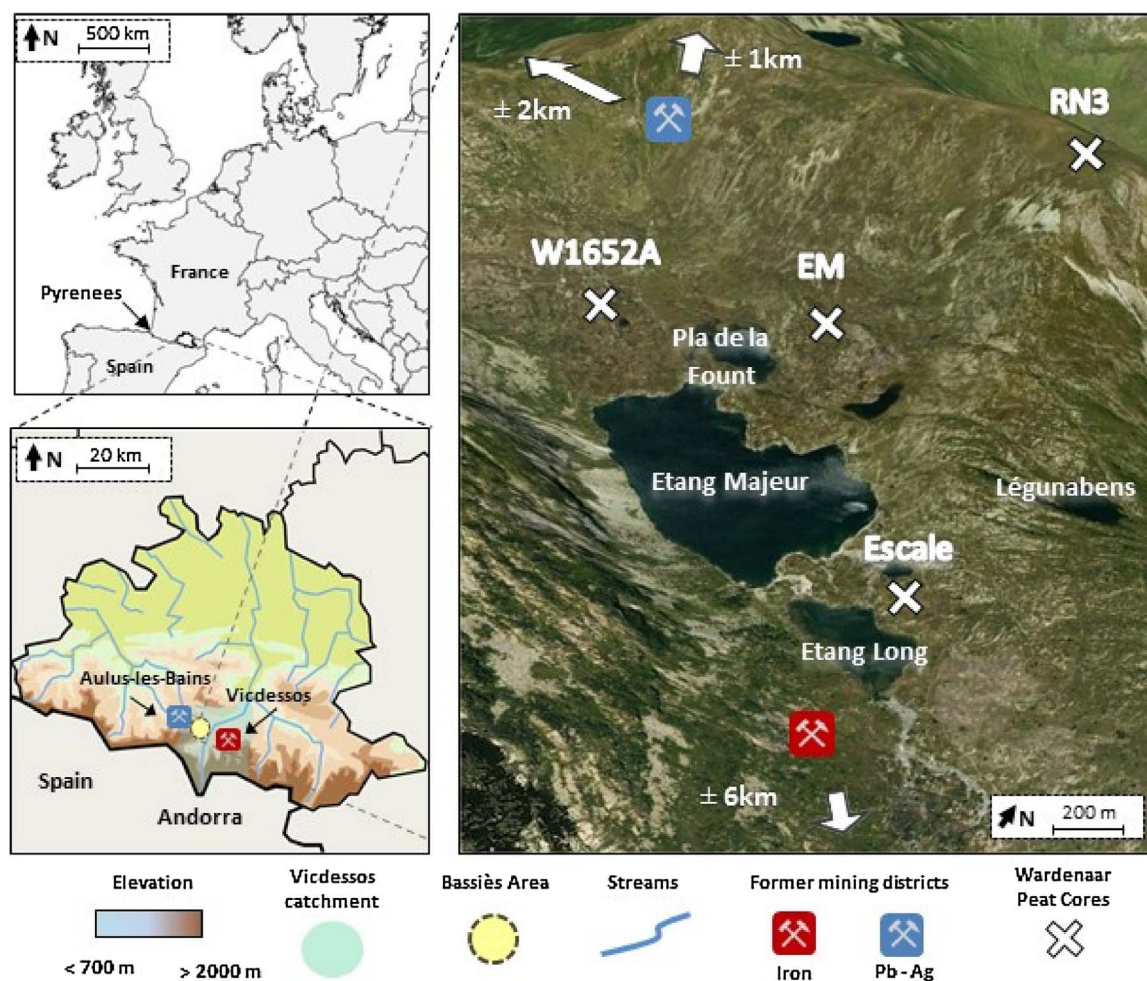


Fig. 1. Study site location within Europe and aerial view of the Bassiès catchment (Pyrénées, FRANCE) including location of the nearest former mines and of the 4 sampled peatlands.

oldest measured sample, i.e. measured calibrated calendar years in the bottom of each core, was 2750–2420 BC, 1190–1000 BC, 990–850 BC, AD 1390–1790 for W1652, EM, Escale and RN3 respectively. Specific information on the peat profiles is reported in Table S2 in SI.

Although the bogs were minerotrophic, as some fluvial input may occur, all peat cores were collected from *Sphagnum*-dominated hummocks with presence of only unsupported lead-210 down to 50–100 cm depth. For this reason, all peat cores should thus be considered as minerotrophic peat with ombrotrophic characteristics. Hummocks at all four sites were sampled from 2010 to 2012, using a Wardenaar corer (Wardenaar, 1987) and prepared following customary protocols (Givelet et al., 2004; Le Roux et al., 2010). Briefly, peat cores were carefully packed in plastic bags in the field, transported back to laboratory and stored frozen until further processing. The cores were then sliced frozen into 1 cm slices using a stainless steel band saw, subsampled with a ceramic knife and then freeze-dried. Finally the samples were milled using an electric mill for organic rich samples and an agate mortar for mineral rich samples.

2.2. Dating and age-depth modelling

Samples dedicated to radiocarbon dating consisted of *Sphagnum* leaves and stems. These were identified and extracted from 1 cm³ of bulk peat following the protocol by Mauquoy et al. (2004). We estimated recent accumulation using ²¹⁰Pb gamma measurements on peat powder. To ensure a valid chronology and correct for any subsurface peaks in ²¹⁰Pb activities related to changes in peat density, or potential downward mobility of ²¹⁰Pb, age-depth models were estimated based

on a combination of both ²¹⁰Pb CRS (Constant Rate of Supply) model (Appleby, 2002) and CLAM radiocarbon age depth model (Blaauw, 2010). Uncertainties of the ²¹⁰Pb ages were calculated using Matlab with MonteCarlo simulations according to Binford (1990) and combined with the radiocarbon uncertainties in CLAM to build a robust age depth model (raw dates and details on age-depth models are reported in SI).

2.3. Geochemistry

Approximately 100 mg of dried and homogenized peat was digested in PFA vials in a clean room using a HF – HNO₃ – H₂O₂ Digestion. The digestion succession protocol is modified from Le Roux and De Vleeschouwer (2010), adding a HCl – HNO₃ step when particles remained. Two certified reference materials of peat (NIMT and NJV-942, recovery data – see Table S4 in SI) were also digested to assure digestion- and analytical quality. All the digestion processes were made using suprapur analytical grade reagents (MERCK®). PHTE were analyzed using a quadrupole ICP-MS (Agilent 7500ce). Pb isotopes (²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb) on peat samples were analyzed using a High Resolution ICP-MS (Thermo Element II XR). Individual sample bracketing with certified NIST NBS-981 was done to correct for mass shift according to Krachler et al. (2004). Blank values were negligible and measurements of CRM NIMT and NJV-942 were in good agreement with certified values for Pb, Sb and Cu, and Pb isotopes (See Table S4 in SI). Some Pb isotopes were also measured on local ores from the Aulus-les-Bains mining district, using a Thermal Ionization Mass Spectrometer (TIMS) without any spiking method (for inter-comparison between the two

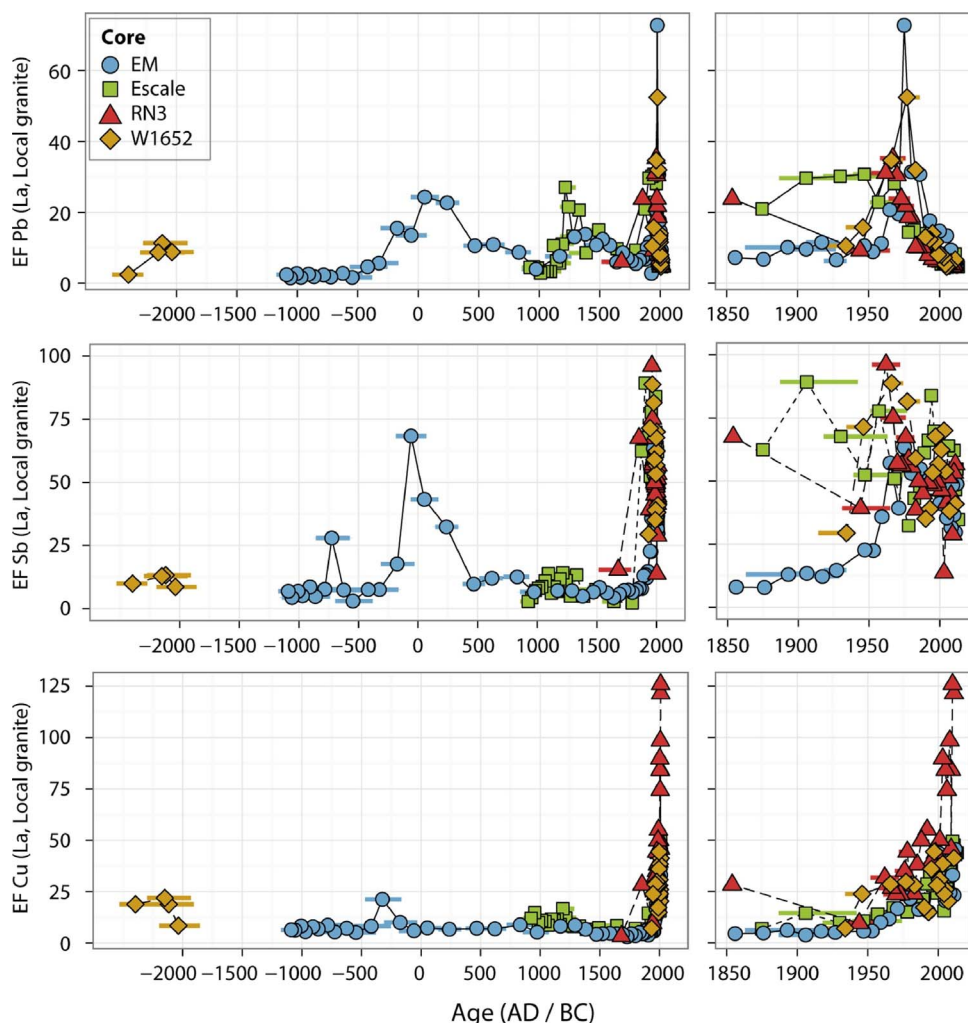


Fig. 2. Enrichment Factors of Pb, Cu and Sb relative to La (as the reference lithogenic element) and the local Bassiès Granite (as the reference material) against time in the 4 sampled cores. Horizontal bars represent the 95% confidence interval from CLAM age-depth model.

methods, see SI and Krachler et al., 2004). Repeated measurements of NIST NBS 981Pb reference material yielded a reproducibility (2 x standard deviations) better than 0,002% for the reported Pb isotopes ratios (data and details are reported in SI).

2.4. Geochemical tools

Enrichment Factor (EF) is a simple geochemical indicator tool, which helps define an enrichment relatively to a reference value, and it has been widely used in different research areas (Camarero et al., 1998; Martínez Cortizas et al., 2002). PHTE ratio to Lanthanum (La) in the local rock (Bassiès Granite) was here used to calculate EF (Eq. (1)) as La is immobile within peatland profiles and few anthropogenic sources are present.

$$EF_{PHTE} = \frac{[PHTE]_{Sample}/[La]_{Sample}}{[PHTE]_{Granite}/[La]_{Granite}} \quad (1)$$

Accumulation rates (AR) of elements (in $\text{mg m}^{-2} \text{yr}^{-1}$) were calculated (Eq. (2)) using peat bulk density (BD in g cm^{-3} ; Givélet et al., 2004), PHTE concentration ([PHTE] in mg kg^{-1}), the thickness of the slice (H in cm) and the age of the slice:

$$AR_{PHTE} = \frac{10 * [PHTE] * H * BD}{Age} \quad (2)$$

3. Results and discussion

3.1. Geochemical background

The local geochemical background was estimated from the oldest samples measured in the deepest layers of EM (dated from 1100 to 920 BC to 920–750 BC) and W1652 (2260–2520 BC) cores. Background Pb AR in W1652 ($32 \mu\text{g m}^{-2} \text{yr}^{-1}$) was comparable to those measured in northern Spain before 1775–1670 BC (Pb AR = $32 \pm 30 \mu\text{g m}^{-2} \text{yr}^{-1}$; (Kylander et al., 2005) and in the range of other European records (Pb AR = $1\text{--}40 \mu\text{g m}^{-2} \text{yr}^{-1}$; Shotyk et al., 1998; Klaminder et al., 2003; Le Roux et al., 2005). In the oldest samples of the EM core (*i.e.* from 1190 – 1000 BC/1000 BCE to 930–660 BC), EFs were stable and already enriched compared to local granite (EF Pb = 2 ± 1 ; EF Cu = 7 ± 1 ; EF Sb = 6 ± 2 ; $n = 7$) and Pb ARs were higher than background European AR (Pb AR = $0.5 \pm 0.1 \text{ mg m}^{-2} \text{yr}^{-1}$). Antimony background AR in the W1652 core (Sb AR = $0.6 \mu\text{g m}^{-2} \text{yr}^{-1}$) was comparable to Sb AR in Swiss Jura (Shotyk et al., 1996) and Black Forest (EGR Sb AR = $0.60\text{--}0.67 \mu\text{g m}^{-2} \text{yr}^{-1}$ around 2410–1840 BC and Sb AR = $1.3 \mu\text{g m}^{-2} \text{yr}^{-1}$ at 1050 BC; Black Forest Sb AR = $0.76\text{--}0.81 \mu\text{g m}^{-2} \text{yr}^{-1}$ 1260–1090 BC), but lower than in the EM core (Sb AR = $8 \pm 1 \mu\text{g m}^{-2} \text{yr}^{-1}$). A small fluvial deposition of local soil could explain these higher background values of PHTE AR in the EM core, as any atmospheric source would likely have impacted and been seen at all sites. Lead isotopic ratios in the oldest samples of EM core were 1.197 ± 0.001 in $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.062 ± 0.002 in $^{208}\text{Pb}/^{206}\text{Pb}$ ($n = 4$), which is typical for granite signatures and similar with other pre anthropogenic records in Europe (Shotyk et al., 1996; Monna et al., 2004b).

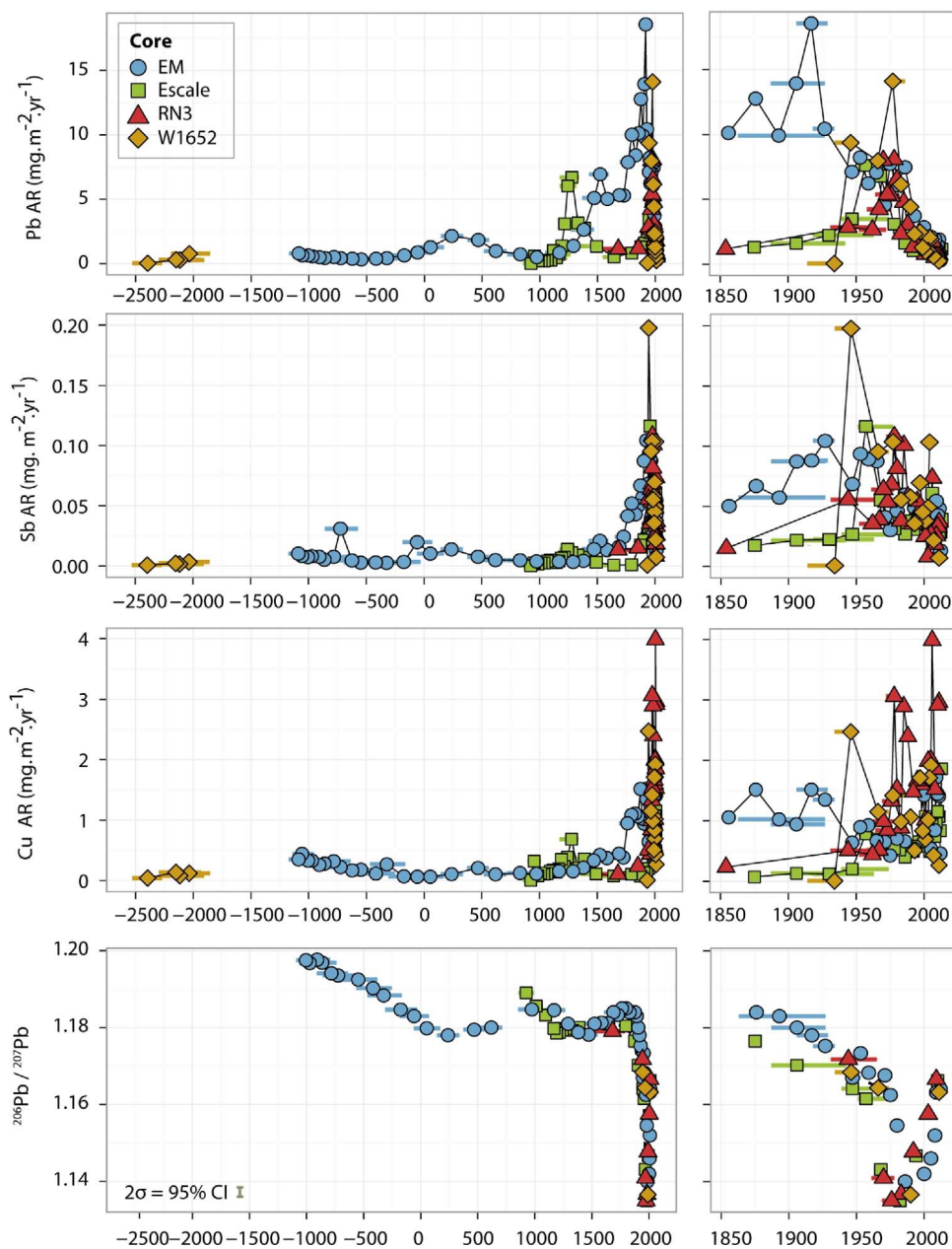


Fig. 3. Accumulation Rates (AR in $\text{mg m}^{-2} \text{yr}^{-1}$) of the PHTE and $^{206}\text{Pb}/^{207}\text{Pb}$ against time in the 4 sampled cores. Horizontal bars represent the 95% confidence interval from the CLAM age-depth model.

3.2. Contamination and metal accumulation over 2500 years

Pb contamination first occurred during the Iron Age and the Roman period from 600 BC to AD 500 as evidenced by a fivefold Pb AR increase and a shift in Pb isotope ratios towards anthropogenic signatures related to mining activities ($^{206}\text{Pb}/^{207}\text{Pb} = 1.179 \pm 0.001$, $\text{AR} = 2.0 \pm 0.2 \text{ mg m}^{-2} \text{yr}^{-1}$, AD 140–330 to AD 280–560, $n = 2$, Figs. 2–5). A Pb EF increase up to 25 in a peat layers dated from 60 BC/AD 170 to AD 140 – 330 confirms the widespread Pb contamination during the Antiquity, which is in good agreement with other European studies (Forel et al., 2010; Küttner et al., 2014). Sb AR and EF trends were synchronous with Pb evolution, showing the intimate relationship between these two PHTE. This is not the case of Cu which show no peak of contamination except a single pulse dated to 480–180 BC. Total inventories of PHTE throughout 400 BC to AD 500 in the EM core were 1.5–5 fold higher for Pb and 1 to 2 fold higher for Sb compared to Black Forest, Swiss Jura or Xistral mountains (Table 1 and Table S1 in SI). The presence of Sb enrichment and such high Pb accumulation (Shotyk et al., 1998; Forel et al., 2010) compared to other European records suggests a regional influence on the deposition (aeolian

and/or fluvial) and PHTE input. The beginning of exploitation of local ores from Les Argentières mine is dated 366 to 192 cal BC (Py-Saragaglia et al., 2017). However, the Pb isotope signature of the Les Argentières ores (i.e. $^{206}\text{Pb}/^{207}\text{Pb} = 1.171 \pm 0.001$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.099 \pm 0.001$, $n = 3$) does not match with the signature in the peat layers (Munoz et al., 2016). Instead the peat is closer to the signature of widespread Roman contamination (i.e. $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.179$; Forel et al., 2010) as well as to several local ores from the Aulus-les-Bains mining district whose exploitation is mainly focused to the Middle Ages (i.e. $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.179$, see SI 5). Thus our findings do not allow identification of the local source of PHTE from ancient mining since we cannot exclude regional sources (i.e. the medieval mines could have been exploited earlier) or even contamination from Spanish Phoenician and Roman mines.

From AD 730–950 to AD 1070–1290 a decline in Pb and Sb contamination occurred as shown by a decrease in the EF (Pb EF = 7, Sb EF = 9), AR (Pb AR = $0.6 \pm 0.1 \text{ mg m}^{-2} \text{yr}^{-1}$, Cu AR = $0.15 \pm 0.02 \text{ mg m}^{-2} \text{yr}^{-1}$, Sb AR = $4.5 \pm 0.7 \mu\text{g m}^{-2} \text{yr}^{-1}$, $n = 3$) and a shift in isotope composition of Pb to more radiogenic values ($^{208}\text{Pb}/^{206}\text{Pb} = 2.083 \pm 0.002$ and $^{206}\text{Pb}/^{207}\text{Pb} = 1.185 \pm 0.001$). Lead

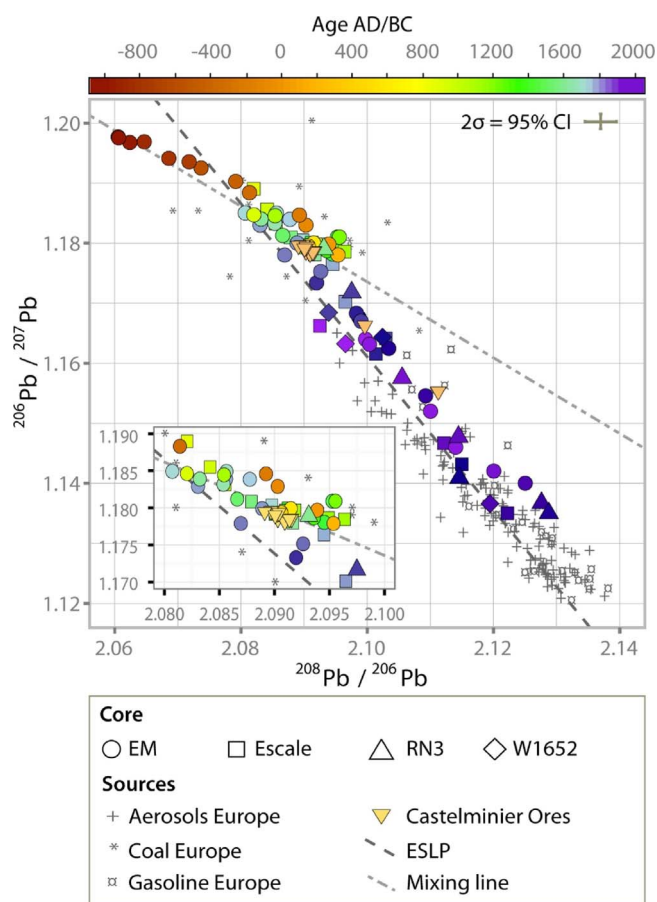


Fig. 4. Lead isotope ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ as measured in the 4 studied cores (circle, square, triangle and diamond for EM, Escale, RN3 and W1652 respectively). Symbols are color coded against the age of each sample with a continuous color scale (top). For comparison, data on ores from the Aulus-les-Bains mining district (downward triangle; See Table S5 in SI) is presented. For comparison with recent lead deposition, European Standard Lead Pollution (ESLP; Haack et al., 2002, 2003) as well as data for Coal, Aerosols and leaded gasoline (Carignan and Garipey, 1995; Monna et al., 1997; Kober et al., 1999; Véron et al., 1999; Chiaradia and Cupelin, 2000; Díaz-Somoano et al., 2009) is also shown.

and Sb AR, as well as Pb isotopic ratios, in the Escale core show comparable values during the same period (Pb AR = 0.4 ± 0.3 ; Sb AR = 3.0 ± 1.3 ; $n = 6$; $^{206}\text{Pb}/^{207}\text{Pb} = 1.186 \pm 0.003$; $^{208}\text{Pb}/^{206}\text{Pb} = 2.084 \pm 0.002$; $n = 3$), and although the Pb contamination is lower, EF and AR do not return to initial levels.

Lead contamination during Middle Ages was identified in the EM and the Escale cores by increases in Pb EF and Pb AR, and a shift in Pb isotopic composition (Figs. 2 and 3). Although the maximum Pb EF appears earlier in the Escale core (Pb EF = 27, AD 1130–1250) than in the EM (Pb EF = 13, AD 1290–1500), the overall timing of higher Pb EF is comparable (i.e. AD 1200–AD 1610 for the EM core and AD 1130–AD 1650 for the Escale one). Contamination is shown to increase continuously since the late Middle Ages in peat cores from Spanish mountains (Martínez Cortizas et al., 2002), Vosges and Alps (Shotyk et al., 1998; Forel et al., 2010) and also at high latitudes as evidenced by lakes sediments (Brännvall et al., 1999) and ice cores (Zheng et al., 2007). Apart from global trends, localized Middle Ages contamination was evident in some mining districts with the example of Black Forest in Germany (Le Roux et al., 2005). Pb inventories throughout AD 1200–AD 1600 were of 1000–1400 mg m^{-2} in the Bassiès cores, which is comparable to the Black Forest accumulation but five times higher than in the Swiss Jura (Shotyk et al., 1998). Such increase in EF and AR in the EM and the Escale cores clearly highlight a local contribution to the Pb contamination. Moreover, the Middle Ages contamination shows comparable Pb signatures in the EM and Escale cores

($^{206}\text{Pb}/^{207}\text{Pb} = 1.179 \pm 0.001$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.095 \pm 0.001$ in the EM Core, $n = 3$; $^{206}\text{Pb}/^{207}\text{Pb} = 1.179 \pm 0.001$ and $^{208}\text{Pb}/^{206}\text{Pb} = 2.093 \pm 0.002$ in the Escale core, $n = 3$). The local contribution to this contamination is highlighted by similar isotope ratios in local ores sampled in the district of Aulus-les-Bains and Laquorre mines (Fig. 1; Munoz et al., 2016). Their values ranged from 1.1782 ± 0.0003 to 1.1797 ± 0.0003 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.089 ± 0.002 to 2.092 ± 0.002 (with the exception of samples 6 and 7, see Table S5 in SI and Fig. 4). The Aulus-les-Bains district is located only 3 km west of the Bassiès valley and the mining activities there, i.e. maximum mining exploitation and metal production, have been dated to the 14–15th centuries. According to ancient texts, this district is known for being active around AD 1320–1340 and for selling about 40 tons of Silver for coinage (Verna, 1996), thus suggesting a large quantity of metal production and a large ore smelting activity within a short time period. As westerly winds passing over Aulus-les-Bains, and then Bassiès are the major winds in the valley (>40% in frequency over in 2013–2015, see Fig. S4 in SI) this strongly suggests that atmospheric PHTE-bearing aerosols, generated by the Aulus-les-Bains mining and metallurgical activities, could have been transported and deposited into the Bassiès catchment.

From about AD 1600 to AD 1950 (Fig. 3) the accumulation of PHTE shows high discrepancies between cores. High AR of 3 PHTE are observed within the EM core (i.e. Pb AR = $12 \pm 3 \text{ mg m}^{-2} \text{ yr}^{-1}$; Sb AR = $0.07 \pm 0.02 \text{ mg m}^{-2} \text{ yr}^{-1}$; Cu AR = $1.2 \pm 0.2 \text{ mg m}^{-2} \text{ yr}^{-1}$, $n = 8$ from AD 1740–1860 to AD 1920–1940) and are associated with low EF. On the contrary, the PHTE accumulation in the Escale, W1652A and RN3 cores shows a continuous increase from the 20th century. Accumulation rates were 5–10 fold lower (Pb AR = $1.1 \pm 0.5 \text{ mg m}^{-2} \text{ yr}^{-1}$; Cu AR = $0.09 \pm 0.03 \text{ mg m}^{-2} \text{ yr}^{-1}$; Sb AR = $0.01 \pm 0.01 \text{ mg m}^{-2} \text{ yr}^{-1}$, $n = 4$ from AD 1650–1680 to AD 1870–1920) during the 19th century followed by a continuous increase of AR and EF. The increase in Pb and Sb deposition observed in the Escale core is consistent with increases observed in other cores across Europe, which were linked to an onset of contamination related to industrialization (Shotyk et al., 1996; Cloy et al., 2005).

The recent overall Pb AR and EF trends are similar, decreasing (by a factor 10) from the 1960–1990s to the present day in the four cores. By comparison, Cu AR and EF shows a continuous increasing trend. This is in agreement with trends observed at French and European scale in moss surveys (Harmens et al., 2010, 2015) as well as other recent peat accumulation records across Europe (Cloy et al., 2009; Olid et al., 2010). Overall, PHTE inventories were low compared to reported European values (Rausch et al., 2005; Olid et al., 2010; See Table S1 in SI). These findings suggest a distal recent contribution of PHTE deposition onto Bassiès peatlands, which is further supported by the Pb isotopic ratios shift to non-radiogenic values ($^{206}\text{Pb}/^{207}\text{Pb} = 1.137 \pm 0.002$; $^{208}\text{Pb}/^{206}\text{Pb} = 2.124 \pm 0.004$) around AD 1960–1990 before shifting to more radiogenic values in the surface samples (i.e. AD 2010–2012; $^{206}\text{Pb}/^{207}\text{Pb} = 1.165 \pm 0.002$; $^{208}\text{Pb}/^{206}\text{Pb} = 2.098 \pm 0.004$, $n = 4$). The contribution of global contamination due to the widespread industrialization and the use of leaded gasoline is supported by the agreement between isotopic ratios in our samples and the ESLP (European Standard Lead Pollution; Haack et al., 2002, 2003). By comparing the isotopic ratios of aerosols and leaded gasoline, our isotopic ratios show a mix between leaded gasoline and other industrial sources with the highest contribution of leaded gasoline occurring throughout 1960–1990 (Monna et al., 1997; Véron et al., 1999; Bollhöfer and Rosman, 2001; See Fig. 4).

3.3. Variability of the accumulation in time and space

Total inventories of Pb and Sb for the period 1950–2015 (Table 1) follow a decreasing trend between the cores in the order of W1652 > EM > Escale > RN3, with less than a two-fold difference between highest and lowest inventories. Bindler et al. (2004) showed that a factor up to 2 could be found between cores within the same peatland due to within site variability in peat characteristics (Bindler et al., 2004;

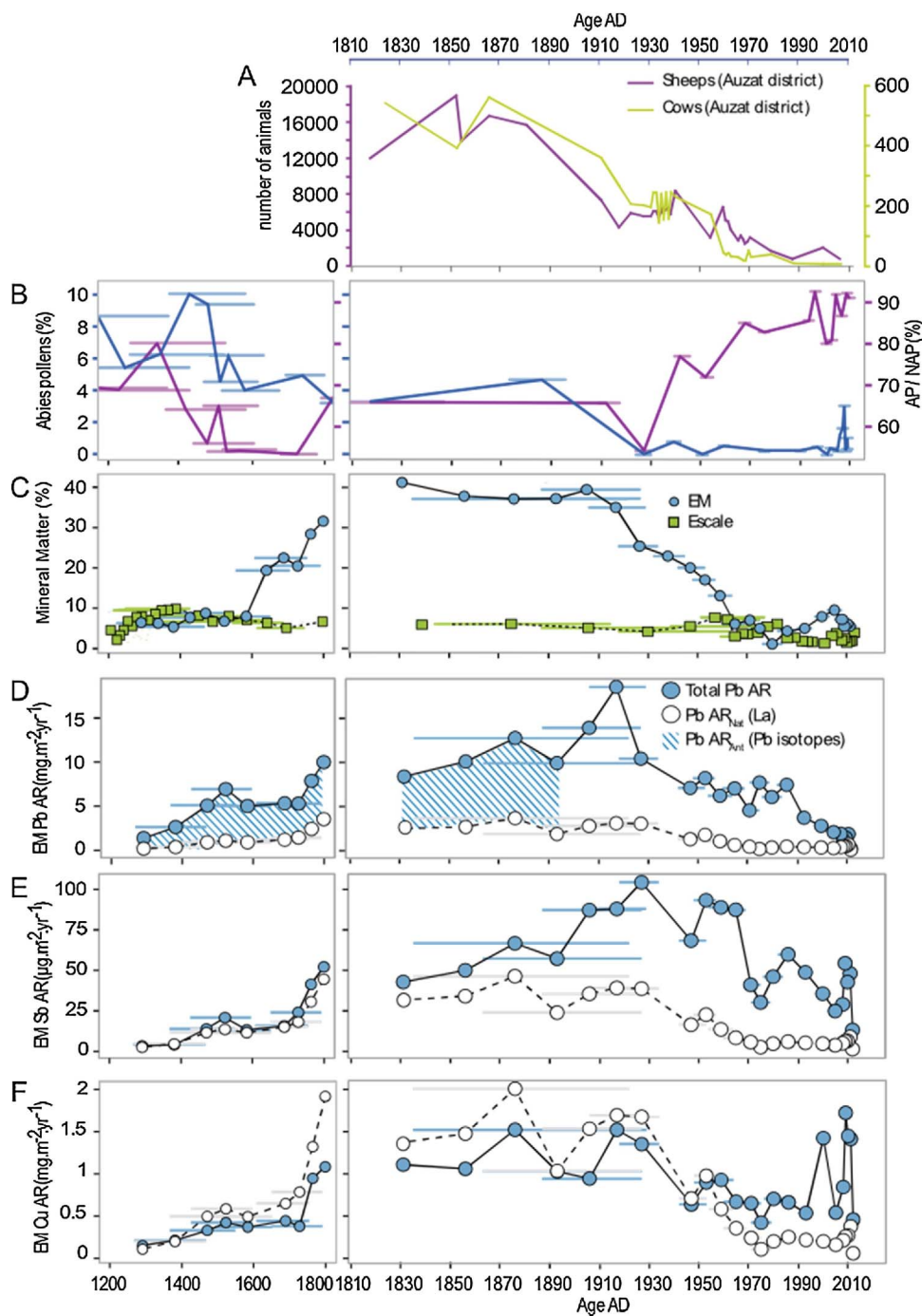


Fig. 5. Recent changes in Bassiès valley, A) Evolution of grazing pressure in the Auzat commune from agricultural statistics, B) *Abies* pollens (%) and AP/NAP (Arboreal Pollen grains/Non-Arboreal Pollen grains in%) from the Orry de Theo mire C) Mineral Matter content (%) from 2 of the Bassiès cores (i.e. EM and Escale) D) E) and F) Total AR, Estimated Natural AR in the EM core (from PHTE/La ratio in the Bassiès Granite and EM core deep samples) of Sb, Cu and Pb and Estimated anthropogenic Pb (from isotope ratios). Horizontal bars represent the 95% confidence interval from CLAM age-depth models, left column shows changes over the period 1200–1800 CE, whereas the right column shows the period 1810–2010 CE at a higher resolution.

Hansson et al., 2013). Yet, for the Escale and the EM core, PHTE accumulations were also comparable throughout AD 1000–1600. A study on Pb and Ti accumulation in *Sphagnum* shows that even a higher variability between AR could be observed between samples from the same site (i.e. 5.6–7.8 ×) due to a difference in *Sphagnum* production rates (Kempter et al., 2010). The variation in accumulation between the 4 studied cores may therefore be interpreted as a difference in the uptake of PHTE, connected to either peat characteristics and/or potential fluvial input, rather than differences in atmospheric deposition. Cu inventories from 1950 in RN3 core were approximately twice as high as in the others cores. There was also a factor of ~2 between the minimum and maximum total inventories but appearing in the order RN3 > W1652 > EM3 > Escale. The order was the same as for Pb and

Sb inventories except that RN3 had higher inventories rather than the lowest. These inventories associated with higher Cu EF in RN3 core suggest that a specific unidentified process is involved in the Cu accumulation, possibly connected to localization as RN3 was the only core on a ridge, 300 m above the others. Enhanced deposition of aerosols due to orographic enhancement is documented (Weathers et al., 2000; Likuku, 2006) but there is no reason for Cu to be the only element concerned by this process, thus Cu AR should be interpreted carefully. It is therefore clear that PHTE accumulation in mountain environments needs further investigations in order to fully understand the local, regional and atmospheric parameters that influence the hotspots of PHTE accumulation in these diverse landscapes (Le Roux et al., 2016).

3.4. Influence of mineral matter on the accumulation of PHTE in the EM core

During the last 5 centuries, the EM core mineral matter content was above 10%, (*i.e.* AD 1580–1730 to 1949–1958, Fig. 5) with a peak at up to 40% (AD 1770–1890). PHTE inventories therefore differ greatly between the EM and Escale peat records (*i.e.* by a factor 10, Table 1). It is not likely that this amount of PHTE was delivered by atmospheric deposition; *i.e.* atmospherically deposited on the EM peatland but not on the Escale located 500 m eastwards, hence we suggest that fluvial derived erosion of the surrounding soils is responsible for such high lithogenic amounts in the EM mire.

Rocks and soils contain trace amount of PHTEs included in their minerals. High amount of mineral matter deposition to peatlands could lead to accumulation of natural PHTE. In Fig. 5, natural AR of PHTE to the EM core has been estimated based on the PHTE ratios to La in the two oldest samples of the EM core, calculated by using the equation (Eq. (3)) below:

$$PHTEAR_{(litho)} = \frac{PHTE}{La_{(litho)}} \times LaAR \quad (3)$$

Using this equation, the estimated lithogenic Sb AR were in good agreement with total Sb AR (calculated using Eq. (2)) except throughout periods of Sb contamination; *i.e.* 250 BC – AD 20 to 380–560 AD and AD 1660 – 1800 to 1770–1890; see Fig. 5). Total AR began to increase from estimated lithogenic Sb AR around AD 1770 – 1890 in the EM core, which corresponds to recent Sb contamination in the Escale core (*e.g.* AD 1830–1910). Estimated lithogenic Cu AR trends were comparable with total Cu AR although they were consistently higher by a factor 1.2–1.5 ($R^2 = 0.63$, $p < 0.05$, $n = 17$), until the recent increase in Cu contamination. This suggests that mineral deposition to the EM mire, either fluvial or aeolian, has led to a greater accumulation of “natural” PHTE, explaining the differences in the accumulation of Cu and Sb between the Escale and the EM cores. Pb estimated lithogenic contribution were in good agreement with total Pb AR before the Antiquity contamination as well as between the Antiquity and the medieval contamination. However, our result show Pb AR which are 5 to 10 fold lower than the total Pb AR during the erosive period. This demonstrates that another source has contributed to the Pb accumulation from AD 1580–1730 to 1949–1958 in the EM peatland. Inventories of Anthropogenic PHTE have therefore been calculated and are reported in Table 1. About 600 mg m⁻² of Pb, 300 mg m⁻² of Cu and 10 mg m⁻² of Sb were directly linked to erosive deposition of lithogenic PHTE from the surrounding soils throughout AD 1600 to AD 1950. These high contributions of lithogenic PHTE to the total inventories (*i.e.* 62% for Sb and 100% for Cu) highlight the influence of detrital mineral matter to the high accumulation of PHTE in peatlands.

3.5. Remobilization of ancient stored Pb

Organic soil erosion has been shown to be a source of stored contaminants (*i.e.* Pb) to lakes in Bassiès valley (Bacardit et al., 2012), especially Pb stored from leaded gasoline contamination over the last century, contributing to contamination up to present time (Bacardit and Camarero, 2010). From the Middle Ages to AD 1900 – 1930, the Pb isotope ratios in the EM core were aligned between two end-members that were the signature of Aulus-les-Bains mining district ores and the signature of the bottom of the EM core used as the natural reference (Fig. 4). It supports our conclusion that the high amount of Pb accumulated in the peat is a mix between these two sources. We used the ²⁰⁶Pb/²⁰⁷Pb ratio in the bottom of EM core and Aulus-les-Bains ores mean ratios to calculate anthropogenic (Pb AR_{Ant.}) and natural contributions to Pb accumulation using the equation (Eq. (4)) below (the Pb AR_{Ant.} is reported in Fig. 5):

$$Pb \ AR_{Ant.} = Pb^* \left(\frac{{}^{206}Pb/{}^{207}Pb_{Sample} - {}^{206}Pb/{}^{207}Pb_{Nat.}}{{}^{206}Pb/{}^{207}Pb_{Sample} - {}^{206}Pb/{}^{207}Pb_{Ant.}} \right) \quad (4)$$

Estimated anthropogenic contributions (*i.e.* Pb from the Aulus-les-Bains ores) range from 83 to 100% throughout AD 1200–1600 and 64–84% from AD 1580–1730 to AD 1920–1936. This timing is synchronous with the erosive supply to the EM core and corresponds to a period of very low atmospheric contamination in the Escale core. It suggests that Pb from Aulus-les-Bains atmospheric contamination (*i.e.* AD 1200–1600), stored in surrounding soils, was remobilized by erosive processes to the EM mire at the same time as the lithogenic PHTE. Moreover, the difference between total Pb AR and Pb AR_{Ant.} is in good agreement with the estimation of natural Pb from background Pb/La ($r^2 = 0.92$, $p < 0.05$, $n = 11$). It justifies the use of EM background isotopic ratios and Pb/La Ratio for the estimation. The contribution of Aulus-les-Bains mining district Pb to total Pb AR from AD 1900–1930 to AD 1950–1960 could not be deducted as the isotopic ratios were no longer aligned between the two end members. However, the beginning of the shift from the mixing line fits with the onset of atmospheric Pb contamination found in the other records of Bassiès valley (*i.e.* the beginning of the 20th century).

The total Pb inventories and the overall timing of Aulus-les-Bains mining district contamination were comparable between the Escale and EM core from AD 1200 to 1600. Considering that Pb atmospheric contamination from Aulus-les-Bains mining district did not occur after AD 1600 (as observed in the Escale core) we could estimate the inventory of remobilized Pb in EM up to AD 1880 – 1920. The results show that a total of 2400 mg m⁻² of Pb were supplied to the mire by erosive processes with 1800 mg m⁻² of remobilized anthropogenic Pb. Even if the remobilized Pb was not estimated after AD 1880–1920, the amount of remobilized Pb was about one third of the total Pb inventory in EM core (Pb Inv = 6300 mg m⁻²) highlighting the importance of soil remobilization in PHTE accumulation

3.6. Importance of ancient atmospheric contamination onto PHTE accumulation

To show the importance of ancient anthropogenic contamination (*i.e.* AD 1800 and the first contamination around 500 BC), the pre-industrial contribution to the total anthropogenic PHTE inventories were estimated. Anthropogenic inventories were calculated by subtracting natural inventories following Eq. (3). An approximation can be made coupling the anthropogenic inventories in the Escale core after AD 1000 (as remobilization occurred in the EM core) to the EM core prior to AD 1000. Estimated anthropogenic atmospheric accumulations prior to AD 1800 were about 85% for Pb, 60% for Sb and 69% for Cu. Contamination of Sb and Pb after AD 1800 is lower than other European records, suggesting that the Bassiès valley was recently nearly isolated from atmospheric contamination. On the contrary, Middle Ages contamination (for Pb only) and Antiquity contamination appears to be higher than in other European records. It underlines the importance of past mining activities to the PHTE deposition and inventories over time, even in such isolated valleys. Such high pre-industrial contributions to the total PHTE accumulation are found elsewhere in mountain environment with variable contributions (*i.e.* 30 to 78% for Sb and 30 to 65% for Pb; see Table 1 and references therein) with the lowest contributions for places like Swiss Jura that are more isolated from local sources of contamination. These findings highlight the variability of accumulation histories in mountain environments and the close relationship between local activities and PHTE accumulations.

3.7. Linking local history to PHTE remobilization

The Bassiès valley was impacted by intensifying grazing activities from the late Neolithic to the 1960s, compared to only low pressure from grazing at present times. Erosive processes have been linked to

sheep and cows grazing in Orry de Theo mire (close to the EM bog, Fig. 1) from AD 1800 to AD 1960 (Galop et al., 2011). During the 19th century, cattle and sheep livestock with up to 500 and 20000 animals respectively were reported for the Auzat district (in which Bassiès valley is one of the high altitude pastures). These livestock were responsible for intense soil erosion that was eventually reduced by the abandonment of intense agro-pastoral activities in the 1960s. This also led to a reforestation of the Bassiès valley by trees (*Betula*, *Pinus*) and shrubs (*Juniperus*, *Calluna*; Galop et al., 2011). Intense erosion to Etang Mort as recorded in the EM core (i.e. mineral matter content up to 40%; Fig. 5) shows a positive relationship with both the intense grazing activities and the decrease in erosion from the 1950's when a change in agro-pastoral practices occurred. The maximum intensity of forest clearing is highlighted by a minimum ratio between Non-Arboreal pollen grains (NAP) and Arboreal-pollens grains (AP) (55–65% from AD 1470–1610 to 1920–1930) which is consistent with decreased presence of pollens from high altitude arboreal vegetation such as *Abies* trees (4–5%). The timing of increased erosion and remobilization of Pb is consistent with the coevolution in the Orry de Theo bog. Agro pastoral practices have induced intense erosion leading to lithogenic PHTE accumulation (especially for Sb and Cu) but also to a remobilization of Pb stored in surrounding soils.

4. Conclusions

Our results presented here clearly emphasize that human activities in the surroundings of Bassiès valley had a great influence on the accumulation of PHTEs in the watershed. Local ancient anthropogenic activities (i.e. Middle Ages) have dispersed PHTE (especially Pb) through the atmosphere by mining and metallurgy, and enhanced the terrestrial dispersion of natural and previously stored PHTE by intensive agro-sylvo-pastoral activities. This remobilization of PHTE represented a large portion of the total PHTE inventory, suggesting that terrestrial transfers were important and acting as hotspots of accumulated contaminants to downstream mires many years after the atmospheric contamination occurred. This clearly shows the long legacy of human-environment interaction and that human activities have impacted the surrounding environment on centennial to millennial scales.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ancene.2017.09.002>.

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