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1 **The Legacy of Metallurgical Atmospheric Contamination in a Mountainous**  
2 **Catchment: A Delayed Response of Pb Contamination**

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7 **Keywords:** Pb contamination, ore smelting, soil remobilisation, contaminant legacy, Pb  
8 inventories

9 **Abstract**

10 Metal-rich fumes emitted during ore smelting contribute to widespread anthropogenic  
11 contamination. Environmental archives (such as lake sediments) record fallouts deposited on  
12 lake and terrestrial surfaces during ancient mining and smelting activities. However, very few  
13 is known about the potential buffering effect of soils upon which metal falls out, prior to be  
14 released through runoff and or/erosion, hence leading to pervasive contamination fluxes long  
15 after the ceasing of metallurgical activities. Here we aim at assessing this long-term  
16 remobilisation in a mountainous catchment area. Lake sediments and soils were collected 7 km  
17 upward a 200-year-old historic mine. The Pb-Ag mine of Peisey-Nancroix was operated  
18 between the 17<sup>th</sup> and the 19<sup>th</sup> centuries with a documented smelting period of 80 years. In lake  
19 sediments, the total Pb content varies from 29 mg.kg<sup>-1</sup> prior smelting to 148 mg.kg<sup>-1</sup> during ore  
20 smelting. Pb isotopes in lake sediments and soils provide evidence of anthropogenic Pb from  
21 the local ore ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.173$ ;  $^{208}\text{Pb}/^{206}\text{Pb} = 2.094$ ) during and after smelting, suggesting  
22 anthropogenic Pb remobilisation for 200 years. The accumulation rates of anthropogenic Pb  
23 calculated in lake sediments after the smelting period confirm such a remobilization. Despite a

24 decrease in this accumulation rate through time, soils still contain significant stocks of  
25 anthropogenic Pb (54-89 % of  $Pb_{ANTH}$ ). The distribution of present-day anthropogenic Pb in  
26 the catchment area depends mainly on topographic characteristics. Coupling lake sediments and  
27 soils investigations is thus necessary to constrain the long-term persistence and remobilisation  
28 of a diffuse contamination related to mining activities.

## 29 **1. Introduction**

30 The mining industry associated with ore smelting is known to threaten Earth's ecosystems  
31 (Hansson et al., 2019; Camizuli et al., 2018; Mariet et al., 2017; Thienpont et al., 2016) through  
32 the dispersion of metal-bearing particles into all compartments of the environment (Hong et al.,  
33 1994; Renberg et al., 1994; Nriagu and Pacyna, 1988). Numerous studies have investigated the  
34 soil contamination in close vicinity of smelting waste storage areas (e.g., Křibek et al., 2016).  
35 However, a substantial amount of metal-bearing particles is also emitted towards the  
36 atmosphere during smelting operations. While most of this atmospheric contamination falls out  
37 in the vicinity of the smelters (Cloquet et al., 2006; Doucet and Carignan, 2001), a significant  
38 fraction of it may spread much further (Brännvall et al., 1997; Hong et al., 1994). One way to  
39 track both the spatial distribution and the timing of past pollution is the use of sedimentary  
40 archives, such as lake sediments (Arnaud et al., 2004; Corella et al., 2021; Guédron et al., 2016;  
41 Sabatier et al., 2014), peatbogs (De Vleeschouwer et al., 2007; Martínez-Cortizas et al., 1999;  
42 Shotyk et al., 1998) or ice cores (Hong et al., 1994; Preunkert et al., 2019; Rosman et al., 2000).  
43 Environmental archives have been widely used for decades to evidence such a contamination  
44 from a regional to a global scale within a long-term perspective (e.g., Mariet et al., 2018). It has  
45 been hence shown that global lead contamination occurred as early as during the Antiquity  
46 period (Brännvall et al., 2001; Shotyk et al., 1998), while the oldest evidence of metal  
47 contamination was dated 4 500 years ago (Leblanc et al., 2000). During the historic period, the  
48 Middle Ages was a second major period of widespread metal contamination in Europe

49 (Brännvall et al., 1999). Since the end of 18<sup>th</sup> century, industrial mining and smelting has  
50 developed, producing large quantities of metal rich-solid wastes and fumes. It has therefore  
51 been possible to establish a worldwide history of metal contamination based on environmental  
52 archives (Renberg et al., 2001; Shotyk et al., 1998). However, this wide picture does not provide  
53 any information about the present-day dispersion and remobilisation within the environment of  
54 ancient metal contaminations. Indeed, mining legacy remains of great concern hundreds to  
55 thousands of years after activities stoppage (Corella et al., 2021; Le Roux et al., 2020; Hansson  
56 et al., 2017; Wiklund et al., 2020), with possible ecotoxicological effects (Camizuli et al., 2018,  
57 2014; Hansson et al., 2019; Monna et al., 2011).

58 Lake sediments may integrate both direct fallouts and catchment-derived fluxes of  
59 contaminating metals. Even when the primary flux has ceased, contaminants stocked in soils  
60 can be remobilised by physical erosion and/or runoff waters, and thus enter the recording  
61 system (i.e., the lake; Sabatier et al., 2014). Although soil represents the largest reservoir of  
62 airborne contaminants (e.g., Pacyna and Pacyna, 2001; Nriagu and Pacyna, 1988), very little is  
63 known about the remobilisation of metals after they originally fell out on soils. The storage of  
64 trace elements within soil has the potential to act as a secondary source of contamination with  
65 a delayed response (Hansson et al., 2019, 2017; Rose et al., 2012; Bacardit and Camarero, 2010;  
66 Yang et al., 2002). At the scale of a catchment area, this should induce a time lag between metal  
67 fallouts into a catchment and their downstream transfer to a lake basin where they could be  
68 stored. However, the lack of data on the duration of ancient mining activities (e.g., Gabrieli and  
69 Barbante, 2014) makes it difficult to assess the potential time-lag between metal emission,  
70 deposition, remobilisation and finally storage in a given lake catchment area.

71 The long-term environmental legacy of ancient mining activities is still poorly documented.  
72 Remote areas such as high mountain catchments are favourable for studying mining activities  
73 far from any urban centre and from other sources of anthropogenic contaminants. This paper

74 aims to test whether soil erosion contributes to the long-term remobilisation of metals deposited  
75 from smelting fumes, in a small valley in the French Alps where mining and smelting occurred  
76 between the 17<sup>th</sup> and the 19<sup>th</sup> centuries. This study combines geochemical and Pb isotopes  
77 analyses of lake sediments and soils from the lake catchment to quantify the amount of  
78 anthropogenic lead deposited and its potential remobilisation or storage over 200 years.  
79 Anthropogenic Pb accumulation rates and inventories were estimated prior, during and after the  
80 smelting period. Finally, these data allow comparing the local anthropogenic Pb flux with the  
81 regional flux.

## 82 **2. Study area**

83 The Peisey-Nancroix Pb-Ag mine is located at 1 500 m a.s.l. in the Ponturin Valley, in the  
84 northern French Alps (Savoy; Fig. 1). The first written evidence of ore extraction at the Peisey-  
85 Nancroix mine and subsequent smelting on site was dated back to the mid-17<sup>th</sup> century (1644  
86 CE; Barbier, 1875). However, industrial installations were implemented in the mid-18<sup>th</sup> century  
87 (1734 CE), and the mine was operated until 1866. During this industrial period, 21 500 t of Pb  
88 and 53 t of Ag were extracted. For at least 80 years (1745-1824), galena (PbS) and Ag-rich  
89 tetrahedrite ((Cu, Fe)<sub>12</sub>(Sb,As,Ag)<sub>4</sub>S<sub>13</sub>) ore was smelted on site, with a great variability in ore  
90 production over decades (Table S1; all supplementary tables, text and figures are referenced  
91 with an S). For pre-industrial (17<sup>th</sup> century) and industrial (18<sup>th</sup> and 19<sup>th</sup> centuries) times,  
92 historical archives written by mining engineers are available. They provide information on the  
93 amount of ore extracted and smelted, on the smelting techniques used, and on the spatial  
94 distribution of the mining and smelting infrastructures. Ore smelting began to decline in 1813  
95 CE, when smelting facilities were relocated in the city of Albertville (35 km as the crow flies  
96 or 65 km down valley from Peisey-Nancroix; Fig. 1B), and was definitively abandoned in 1824  
97 CE. Local contamination of the surrounding hayfields has been engendered by 200-hundred  
98 years of mining and smelting waste storage on the surface (Guillevic et al., 2023).

99 To study atmospheric contaminant emissions during smelting and their subsequent deposition  
100 and transfers, Lake La Plagne and its catchment were selected because the lake is located in the  
101 upper valley of the Ponturin River, 7 km downwind and upward the former Pb-Ag mining and  
102 smelting site (Fig 1C). Lake La Plagne, located at 2100 m a.s.l. in the Vanoise massif,  
103 corresponds to a catchment of 1742 ha with a maximum altitude of 3100 m (Fig. 1D). The upper  
104 valley is only accessible by foot, and only pastoral activities are known in the area. The bedrock  
105 of the catchment consists of metamorphic rocks of the Variscan basement (intermediate to  
106 mafic compositions) and carbonate rocks (marble, dolomite, and alpine dedolomitised breccia  
107 called “cargneules”) from the Mesozoic sedimentary cover (Fig. 1D). A large part of the area  
108 is covered by screes and tills. The alpine meadows are covered with *Rumex alpina*, *Nardus*  
109 *stricta*, *Vaccinium vitis-idea*, *Achillea millefolium* and *Sempervivum montanum*. The waterways  
110 upstream of the 19 m-deep Lake La Plagne cross basement rocks into a peaty-like delta system.  
111 The Ponturin River runs from the outlet of the lake northwards before bordering the ancient Pb-  
112 Ag mining and smelting site of Peisey-Nancroix, 7 km downstream.

113 *Figure 1 should be inserted here (location map)*

### 114 **3. Materials**

#### 115 **3.1 Lake sediments**

116 With the help of a UWITEC gravity corer hammering from a small boat, 5 sediment cores,  
117 PLG-01 (IGSN: TOAE0000000343; 1.52 m), PLG-02 (IGSN: TOAE0000000344; 2.25 m),  
118 PLG-03 (IGSN: TOAE0000000345; 1.06 m), PLG-04 (IGSN: TOAE0000000347; 0.95 cm),  
119 and PLG-05 (IGSN: TOAE0000000349; 2.14 cm), were collected in the centre of Lake La  
120 Plagne (N 45°29'2.709''; E 6°50'29.667'', Fig. 1D) in July 2019. Detailed fieldwork  
121 information can be found at <https://www.cybercarotheque.fr/index.php?mission=PLAGNE>. At

122 the laboratory, each core was split into two halves, one of them was used for the following  
123 analyses.

### 124 **3.2 Surface and subsurface soil samples**

125 A total of 13 surface soil samples were collected with a manual auger at a depth of 0-20 cm  
126 along two altitudinal transects in the lake catchment (Fig.1D). Transect A (n = 5) follows a  
127 southwestern direction from the west of the lake: samples A1 (2170 m), A2 (2177 m), A3 (2330  
128 m), A4 (2402 m), and A5 (2447 m). Transect B (n = 6) points towards the southeast from the  
129 northern side of the lake: samples B1 (2153 m), B2 (2170 m), B3 (2227 m), B4 (2264 m), B5  
130 (2314 m), and B6 (2336 m). Sample B7 (2190 m) was collected between these two transects,  
131 and sample B8 (2149 m) was collected in the lake delta. Additionally, two soil profiles were  
132 dug at the top of each transect (A5 and B6) to retrieve samples from different soil horizons. Soil  
133 samples were air-dried for a few days and sieved to 2 mm before analyses.

## 134 **4. Methods**

### 135 **4.1. High-resolution elemental EDS-XRF analyses**

136 After visual logging and photographing, the relative major (Al, Si, K, Ca, Mg, Ti, Mn, Fe) and  
137 trace (Zn, Pb, As, Rb, Sr, Zr) element contents were measured along the lake sediment core by  
138 energy dispersive spectrometer-X-ray fluorescence (EDS-XRF) using the AVAATECH Core  
139 scanner at the EDYTEM laboratory. A continuous 1-mm step measurement was performed on  
140 a PLG-03 one-half core with multiple runs at 10 kV and 0.2 mA during 15 s, allowing the  
141 detection of lightweight elements, and a second run at 30 kV at 0.15 mA during 20 s to detect  
142 heavy elements. In order to discriminate As and Pb, which suffer from peak overlap, peak  
143 intensities were calculated using only Pb\_L $\beta$  and As\_K $\alpha$ . Argon was also analysed and used as  
144 an element control for the homogeneity of the core. Hierarchical clustering on principal  
145 component analysis (PCA) of major elements was applied to compare visual logging to

146 geochemical units of lake sediment using the multivariate analysis package FactoMineR (Lê et  
147 al., 2008) in R statistical software (R Core Team, 2022).

#### 148 **4.2 Carbonates and organic matter content**

149 The determination of the organic matter and carbonate contents of the lake sediments was  
150 performed by loss on ignition (LOI) on discrete samples from PLG-03 following the method  
151 by Heiri et al. (2001). The weight loss was measured after a first heating step at 550°C (LOI<sub>550</sub>),  
152 providing an assessment of the organic matter content within lake sediments, and after a second  
153 heating step at 950°C (LOI<sub>950</sub>), used as a proxy of the carbonate content.

154 The carbon total content (inorganic and organic fraction, C<sub>T</sub>) of the fine fraction of soils was  
155 measured by dry combustion (ISO 10694), and the CaCO<sub>3</sub> total content (CaCO<sub>3</sub>, ISO 10693)  
156 was measured by the volumetric method at the French national reference soil laboratory  
157 (INRAE, France). Based on the C<sub>T</sub> and CaCO<sub>3</sub> contents, the total organic carbon (TOC,  
158  $TOC = C_T - (0.12 \times CaCO_3)$ ) and the soil organic matter (OM,  $OM = 1.7 \times TOC$ ) were  
159 calculated. The pH of the soil samples was also measured.

#### 160 **4.3 Major and trace element contents, and enrichment factor (EF)**

161 Following the routine analysis of Carignan et al. (2001), soils (< 2 mm; n = 13) and lake  
162 sediment samples (n = 66) were analysed for 54 elements after lithium tetraborate fusion using  
163 ICP–OES iCap6500 (major elements) and ICP–MS iCapQ (trace elements) at the Service  
164 d'Analyse de Roches et Minéraux (SARM-CNRS, Nancy, France). Total concentration  
165 uncertainties were about 1% for major elements and between 5% and 10% for trace elements,  
166 depending on concentration levels. Reference materials and blanks were prepared along with  
167 the samples. Lake sediment sampling along the core was performed approximatively at each  
168 cm according to facies changes for a total of 66 samples for a 106cm core (PLG-03). Sampling  
169 was spaced to avoid thick instantaneous events identified during logging, such as event deposits



170 that were considered instantaneous deposits and non-representative of continuous  
171 sedimentation (Sabatier et al., 2022; Arnaud et al., 2002). In this paper, major and trace element  
172 contents are presented as the median  $\pm$  standard deviation.

173 For both soil and lake sediments, the enrichment factor (*EF*) of potentially toxic trace elements  
174 (PTEs) was calculated to quantify the PTE contamination in comparison to a reference  
175 background:

$$176 \quad EF_{M_1} = \frac{\left(\frac{M_1}{M_2}\right)_{\text{SAMPLE}}}{\left(\frac{M_1}{M_2}\right)_{\text{BKG}}} \quad \text{equation (1)}$$

177 where  $M_1$  is the Pb or As content of the sample and of the reference background (BKG), and  
178  $M_2$  is the content of a selected “conservative” element in soil and lake sediments that has  
179 exclusively a lithogenic origin (Reimann and de Caritat, 2000) and a content on the same order  
180 of magnitude as the studied PTE. Both Rb and Th were tested as conservative lithogenic  
181 elements for the calculus of the *EF*. The classification of *EF* is presented in Table S2.

#### 182 **4.4 Pb isotopes**

183 A selection of lake sediment (n = 9) and all soil samples (surface and subsurface horizons,  
184 n = 20) were analysed for Pb isotopic composition ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) using a  
185 Thermo Fischer Multicollector (MC-ICP–MS) Neptune Plus at the SARM-CNRS laboratory.  
186 After digestion, the samples are placed on an ion exchange resin to chemically separate the  
187 mineral matrix. Lake sediment samples were chosen before the sampling of the continuous 66  
188 discrete samples based on the Pb and As peaks identified on the EDS-XRF profiles. Two  
189 samples (85-86 cm and 103-104 cm) presenting the lowest Pb and As abundances were chosen  
190 to define isotopic composition of the local background.

191 In-situ Pb isotope measurements were performed on 10 to 20 individual galena crystals of two  
192 ore-bearing samples collected on the waste heaps to determine the local ore signature.  
193 Measurements were performed at the CRPG-CNRS (Nancy, France) using the 1270 ion  
194 microprobe in monocollection mode to a mass resolution of 4000, following Deloule et al.  
195 (1986).

#### 196 **4.5 Short-lived radionuclides ( $^{210}\text{Pb}$ , $^{137}\text{Cs}$ , $^{230}\text{Am}$ )**

197 The activities of natural short-lived radionuclides  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^7\text{Be}$  and artificial  
198 radionuclides  $^{241}\text{Am}$  and  $^{137}\text{Cs}$  in lake sediment samples were measured at the Laboratoire  
199 Souterrain de Modane (LSM, France) on EDYTEM-operated low background SAGe well  
200 detectors (Reyss et al., 1995). For each sample, the excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{ex}}$ ) activities were  
201 calculated as the difference between the total  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  activities. The first 30 cm of lake  
202 sediments from the PLG-03 core were sampled according to lithological variations,  
203 approximatively each cm. Using a small cylinder ( $3\text{ cm}^3$ ), the dry bulk density (DBD) was  
204 determined by measuring the dry weight for a constant volume of sediment before analysis.  
205 Short-lived radionuclide data were computed with the serac package (Bruel and Sabatier, 2020)  
206 in R software (R Core Team, 2022) build an age-depth model for the recent sediments.

#### 207 **4.6 $^{14}\text{C}$ dating**

208 Organic macroremains were sampled for  $^{14}\text{C}$  (radiocarbon) dating from cores PLG-01, PLG-  
209 03, PLG-04 and PLG-05, which were correlated from visual observation. Despite difficulties  
210 in providing a proper quantity of macroremains, 13 samples were dried at  $60^\circ\text{C}$  and sent to the  
211 accelerator mass spectrometer (AMS) of the Poznan Radiocarbon laboratory (Poland) to  
212 measure  $^{14}\text{C}$ . The radiocarbon ages were calibrated with the Intcal20 calibration curve (Reimer,  
213 2020) using the clam package (Blaauw, 2010) in R software (R Core Team, 2022) to construct

214 a single age-depth model correlated with short-lived radionuclide measurements ( $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ ,  
 215  $^{231}\text{Am}$ ).

#### 216 **4.7 Anthropogenic Pb ( $Pb_{\text{ANTH}}$ ) and accumulation rate ( $AR_{\text{Pb\_ANTH}}$ )**

217 Two methods were used to measure the anthropogenic Pb ( $Pb_{\text{ANTH}}$ ) of lake sediments and soils:  
 218 elemental and isotopic methods. First, the total Pb content of one sample ( $Pb_{\text{TOTAL}}$ ) is  
 219 considered as the sum of the lithogenic background Pb ( $Pb_{\text{BKG}}$ ) and the anthropogenic Pb  
 220 contents;  $Pb_{\text{TOTAL}} = Pb_{\text{BKG}} + Pb_{\text{ANTH}}$ . To take into account the natural variations related to  
 221 changes in the terrigenous fraction, the lead concentration was normalized to a conservative  
 222 lithogenic element that is not emitted into the atmosphere during smelting, following equation  
 223 (2):

$$224 \quad Pb_{\text{ANTH}} = Pb_{\text{TOTAL}} - \left( Rb_{\text{TOTAL}} \times \left( \frac{Pb_{\text{BKG}}}{Rb_{\text{BKG}}} \right) \right) \text{ equation (2)}$$

225 Second, the calculation of  $Pb_{\text{ANTH}}$  was also determined isotopically using a two end-member  
 226 mixing model, where the mean of the two deepest lake sediment samples represent the  
 227 lithogenic background end-member (85-86 cm and 103-104 cm):

$$228 \quad Pb_{\text{ANTH}} = Pb_{\text{TOTAL}} \times \frac{\left( \frac{Pb^{206}}{Pb^{207}} \right)_{\text{sample}} - \left( \frac{Pb^{206}}{Pb^{207}} \right)_{\text{BKG}}}{\left( \frac{Pb^{206}}{Pb^{207}} \right)_{\text{local\_ore}} - \left( \frac{Pb^{206}}{Pb^{207}} \right)_{\text{BKG}}} \text{ equation (3)}$$

229 The accumulation rate of anthropogenic Pb ( $AR_{\text{Pb\_ANTH}}$ ) represents the annual flux of  
 230 anthropogenic Pb per  $\text{m}^2$ . It was calculated in lake sediments to evaluate changes in metal  
 231 accumulation along the sediment core, and to compare the Lake La Plagne accumulation rate  
 232 to regional fluxes that were estimated at Lake Anterne (Fig1B) during the same time period.  
 233 The  $AR_{\text{Pb\_ANTH}}$  (in  $\text{mg} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ ) was calculated according to equation (4):

$$234 \quad AR_{\text{Pb\_ANTH}} = SR \times DBD \times Pb_{\text{ANTH}} \text{ equation (4)}$$

235 where  $SR$  is the sedimentation rate (or accumulation rate, in  $\text{mm.y}^{-1}$ ) obtained from the age-  
 236 depth model,  $DBD$  is the dry bulk density (in  $\text{g.cm}^{-3}$ ) and  $Pb_{\text{ANTH}}$  corresponds to the  
 237 anthropogenic Pb content (in  $\text{mg.kg}^{-1}$ ). Details on the  $DBD$  calculation of lake sediments and  
 238 the fine fraction of soil ( $< 2 \text{ mm}$ ) are presented in Text S1.

## 239 4.8. Inventory calculations

### 240 4.8.1 Inventories of anthropogenic Pb ( $\text{g.m}^{-2}$ ):

241 The inventory of anthropogenic Pb ( $Inv_{\text{Pb}}$ ) represents the quantity of anthropogenic Pb stored  
 242 per unit area in soils or in lake sediments (in  $\text{g.m}^{-2}$ ). For lake sediments, it is possible to calculate  
 243 the total amount of metal accumulated for the area of the sediment core ( $Inv_{\text{Pb\_lake\_sed}}$ ) following  
 244 equation (5):

$$245 \quad Inv_{\text{Pb\_lake\_sed}} = \sum_{i=1}^n SR \times DBD \times Pb_{\text{ANTH}} = \sum_{i=1}^n AR_{\text{Pb\_ANTH}} \quad \text{equation (5)}$$

246 where  $n$  is the thickness of the accumulated sediment, which represents a time period using the  
 247 age-depth model.

248 For soils, the inventory ( $Inv_{\text{Pb\_soil}}$ ) is calculated following equation (6), with  $T$  being the  
 249 thickness of the soil to integrate:

$$250 \quad Inv_{\text{Pb\_soil}} = T \times DBD \times Pb_{\text{ANTH}} \quad \text{equation (6)}$$

### 251 4.8.2 Inventories of $^{210}\text{Pb}_{\text{ex}}$ ( $\text{Bq.m}^{-2}$ ):

252 The larger the catchment area, the larger the amount of sediment, and therefore the more the  
 253 anthropogenic contaminant is expected to be remobilised (assuming uniform fall-outs). A focus  
 254 factor ( $FF$ ) is calculated to compare inventories of  $^{210}\text{Pb}_{\text{ex}}$  (fine sediment proxy) among lakes:

$$255 \quad FF = \frac{Inv_{\text{Pb}_{\text{ex}}^{210} \text{PLG}}}{Inv_{\text{Pb}_{\text{ex}}^{210} \text{ANT}}} \quad \text{equation (7)}$$

256 with  $Inv. Pb_{ex}^{210}_{PLG}$  the inventory of  $^{210}Pb_{ex}$  in Lake La Plagne (PLG), and  $Inv. Pb_{ex}^{210}_{ANT}$  the  
257 inventory of  $^{210}Pb_{ex}$  in Lake Anterne (ANT). A  $FF > 1$  indicates a net accumulation of sediment.  
258 The  $FF$  will allow calculating the difference in anthropogenic Pb accumulated over a given  
259 period of time and the local surplus of anthropogenic Pb ( $Surplus_{Pb}$  in  $g.m^{-2}$ ) potentially  
260 engendered by smelting activities, following equation (8).

261 
$$Surplus_{Pb} = Inv_{Pb_{PLG}} - FF \times Inv_{Pb_{ANT}} \text{ equation (8)}$$

262 Lake La Plagne was compared to Lake Anterne (Fig. 1B) as (i) its relatively small catchment  
263 area (256 ha) makes it a good atmospheric recorder, and (ii) there was no important  
264 metallurgical activity in the 18<sup>th</sup> and 19<sup>th</sup> centuries nearby, so that it only recorded the regional  
265 atmospheric signal.

## 266 **5. Results**

### 267 **5.1 Sedimentology of Lake La Plagne**

268 As it is often the case in alpine lakes, many event layers are interbedded with the continuous  
269 sedimentation in Lake La Plagne sediment cores. These layers show a coarser grain size at the  
270 base (normal grading) associated with few millimetres size organic debris. They present a beige  
271 or brown yellowish colour contrasting with the dark brown facies characterising the continuous  
272 sedimentation. The correlation between the 5 cores is mainly based on events and is reported in  
273 the supplementary material Fig. S1 A list of the event depths is reported in Table S3 for each  
274 core studied.

275 The continuous sedimentation presents slight changes over the studied sequence and was thus  
276 divided into 4 units based on XRF logging,  $LOI_{550}$  and  $LOI_{950}$  data. Unit 1 (6-11 cm;  
277 25- 45 cm, Fig. 2) consists of a dark brown silt with  $LOI_{550}$  up to 8 wt. % ( $5.1 \pm 1.9$  wt. %),  
278 which is slightly higher than for the other units. The carbonate content estimated based on  
279  $LOI_{950}$  is also the highest among the continuous sedimentation units ( $18.0 \pm 4.6$  wt. %). This

280 induces a lower DBD ( $0.8 \pm 0.2 \text{ g.cm}^{-3}$ ) than for the more silicate-rich units found at depth (Fig.  
281 2). Only the sediment colour allows distinguishing Unit 2 (45-64 cm) from Unit 3 (78-87 cm;  
282 99.5-107 cm), as their LOI<sub>550</sub> and LOI<sub>950</sub> are similar (4.3-4.7 and 9.3-10.6 wt. %, respectively).  
283 The slightly lower organic content of Unit 2 ( $4.3 \pm 1.3 \text{ wt. } \%$ ) may be responsible for its greener  
284 colour in comparison to the brown-dark colour of Unit 3 ( $4.7 \pm 1.3 \text{ wt. } \%$ ). Unit 4 (87-99.5 cm)  
285 corresponds to laminated mixing between Unit 2 and Unit 3.

286 *Figure 2 should be inserted here (lithostratigraphic description of core PLG19-03).*

## 287 **5.2 Major elements**

### 288 *5.2.1 Lake sediments*

289 Three clusters were identified from hierarchical clustering (Fig. S2). The first dimension  
290 (50.73 %) and the second dimension (29.18 %) of the PCA distinguish carbonate-rich top event  
291 layers (cluster 1) and terrigenous continuous sedimentation (clusters 2 and 3). This  
292 classification corroborates the total major element contents (Fig. 2), showing a lower SiO<sub>2</sub>  
293 content ( $22.3 \pm 9.3 \text{ wt. } \%$ ,  $n = 16$ ) and a higher CaO content ( $19.4 \pm 4.1 \text{ wt. } \%$ ) in the  
294 carbonate-rich events compared to continuous sedimentation (SiO<sub>2</sub>:  $39.3 \pm 6.4 \text{ wt. } \%$ ; CaO:  
295  $7.9 \pm 3.3 \text{ wt. } \%$ ,  $n = 53$ ).

296 The continuous sedimentation represented by cluster 2 and cluster 3 encompassed the 4 units  
297 identified during logging as well as the deep event layers (64-78 cm; 87-91 cm; 93-95 cm and  
298 98-99 cm). These deep events, which have a geochemical signature similar to the continuous  
299 sedimentation (Fig. S2), are identified based on their brown-yellowish colour and sandy texture.  
300 Unit 2, Unit 3 and Unit 4 present similar major element contents whereas Unit 1 presents a  
301 higher carbonate content, thus diluting the silicate signal.

### 302 *5.2.2 Soils*

303 Most soils from the Lake La Plagne catchment are developed on basement rocks and/or till with  
304 minor proportions of carbonate fragments, which are abundant in screes (Fig. 1D). These soils  
305 can be classified as rankosols with the exception of sample B8, which is a saturated fluvisoil  
306 with the highest  $\text{CaCO}_{3\text{T}}$  content (5 wt. %, Table 1). The other surface soils are silty-sandy soils  
307 with no carbonates ( $< 1$  wt. %  $\text{CaCO}_{3\text{T}}$ ). The total organic carbon (TOC) content varies from 6  
308 to 12 wt. %. Superficial soils collected on basement rocks and tills (A2, A4, B1, B3, B4, B5  
309 and B6 ) presented a higher  $\text{SiO}_2$  content ( $52.4 \pm 4.5$  wt. %) and a lower CaO and MgO contents  
310 ( $0.7 \pm 0.5$  wt. %; and  $2.3 \pm 0.4$  wt. %; respectively) than the soils overlying the cagneules and  
311 the carbonate-rich screes ( $\text{SiO}_2$ :  $43.9 \pm 3.5$  wt. %; CaO:  $1.6 \pm 2.4$  wt. %; MgO:  $3.8 \pm 1.5$  wt. %;  
312 A1, A3, A5, B2, B7, B8).

313 Surface soils have heterogeneous pH values ranging between 4.5 and 7.6 (Table 1). The most  
314 alkaline soils (pH  $> 7$ ; samples A1, B2, B7 and B8) are located down the slope or along the  
315 slopes with downhill carbonate rock outcrops. The most acidic soils (pH  $< 5$ ; samples A2, A4,  
316 B4 and B5) are developed on basement rocks of the catchment. Soil samples A3, A5, B1, B3,  
317 and B6 present an intermediate pH.

318 *Table 1 should be inserted here (Soil properties and mean major and trace elements)*

### 319 **5.3 Trace elements and enrichment factor**

#### 320 *5.3.1 Lake sediments*

321 Among the elements of metallurgic interest, Pb and As show clear variations according to XRF  
322 scanning. In contrast, Zn, Cu and Ni display weak and noisy signals. No signal was recorded  
323 for Sb despite the presence of Sb-bearing minerals in the ore. The Pb profile shows three peaks  
324 (56.5-58.3 cm, 82.5-79.5 cm, and 62.5-64.5 cm) interspersed with event layers (in red, Fig. 2).  
325 The As profile shows 2 peaks (30-31 cm and 27.9-29.3 cm) also interspersed with an event  
326 layer.

327 The total trace element contents in discrete samples confirmed that apart from Pb and As, the  
328 other potentially toxic trace elements (PTE; Ni, Cu, Sb and Zn) do not display any positive  
329 anomaly. The Ni content varied between 12 and 37 mg.kg<sup>-1</sup> ( $26.7 \pm 4.5$  mg.kg<sup>-1</sup>), the Cu content  
330 varies between 16 and 51 mg.kg<sup>-1</sup> ( $39.3 \pm 5.3$  mg.kg<sup>-1</sup>), the Zn content varied between 69 and  
331 235 mg.kg<sup>-1</sup> ( $182.6 \pm 28.5$  mg.kg<sup>-1</sup>), and the Sb content varied between 1.8 and 4.1 mg.kg<sup>-1</sup>  
332 ( $3.0 \pm 0.4$  mg.kg<sup>-1</sup>). The total arsenic content confirmed the EDS-XRF data, with the As content  
333 varying from 34.7 to 505 mg.kg<sup>-1</sup> ( $87.8 \pm 109.0$  mg.kg<sup>-1</sup>). Simultaneously, for the As peaks, an  
334 increase in the organic matter was measured with LOI<sub>550°C</sub> (between 6 and 8 wt. %, Fig. 2).

335 The total Pb content varies from 29 to 148 mg.kg<sup>-1</sup> for the continuous sedimentation samples  
336 ( $61.5 \pm 30.4$  mg.kg<sup>-1</sup>, n = 54). The deepest lake sediment samples (85 to 106 cm) present a low  
337 Pb content, between 29 and 38 mg.kg<sup>-1</sup>. The highest Pb content was measured between 54 and  
338 85 cm (from 47 to 148 mg.kg<sup>-1</sup>). This confirmed the 3 Pb peaks identified from the EDS-XRF  
339 profile (Fig. 2). From the top of the core to 54 cm, the total Pb content varies between 29 and  
340 87 mg.kg<sup>-1</sup>. The total Pb content of one of the top events (6 to 7 cm) reaches 690 mg.kg<sup>-1</sup>  
341 between 6 and 7 cm (Fig. 2), which is quite surprising considering that no major Pb peak was  
342 identified by EDS-XRF at this depth in any core (Fig S3).

343 The  $EF_{Pb}$  was calculated for each lake sediment discrete sample using for reference background  
344 the mean Pb/Rb ratio of the discrete samples collected between 85 and 106 cm (Pb/Rb:  
345  $0.32 \pm 0.02$ , n = 15), which are considered to represent the local geological background.  
346 Element Rb was chosen over Th as the conservative element because its standard error of the  
347 mean background ratio was lower and because Rb was identified within the terrigenous fraction  
348 (Fig. S2). The enrichment was considered significant for  $EF_{Pb} > 2$ . Table S4 presents  $EF_{Pb}$   
349 values in depth along the sediment core. From 0 to 55 cm, the  $EF_{Pb}$  increases from 2 to 4. From  
350 55 to 62 cm, the  $EF_{Pb}$  is equal to 3, showing a minor enrichment. From 62 to 81 cm, the  $EF_{Pb}$



351 shows a moderate enrichment up to 5. As the deeper sediments are used for background and  
352 reference values,  $EF_{Pb}$  is close to 1 between 85 and 106 cm.

### 353 5.3.2 Soils

354 The Pb content in superficial soil samples varies from 39 to 132 mg.kg<sup>-1</sup> ( $96.2 \pm 28.2$  mg.kg<sup>-1</sup>),  
355 with a high variability depending on the sample location, but no relationships with the  
356 underlying lithologies (Table 1 and Fig. 3). The deepest soil horizons of profiles A5 (overlying  
357 cagneule and dolomite) and B6 (developed on basement-rich tills lying over cagneule and  
358 dolomitic rocks) present equivalent Pb/Th ratios. Despite lithological differences, these deepest  
359 horizons are used as background references to calculate enrichment factors in soils as their  
360 Pb/Th ratios are equivalent (Pb/Th ~ 2.7).  $EF_{Pb}$  in soils varies between 2 and 9 (Fig. 3). Despite  
361 Pb enrichment, the PTE contents (Ni, Cu, As, Sb) of surface soil samples are very low and  
362 therefore show no significant enrichment (Table 1). The depth transfer of Pb is limited; only  
363 the first two horizons of profiles A5 and B6 show moderate to severe Pb enrichment whereas  
364 the deeper horizons display no enrichment (Table S5).

## 365 5.4 Pb stable isotopes

### 366 5.4.1 Local ore

367 The local galena displays  $^{206}Pb/^{207}Pb$  ratios of  $1.172 \pm 0.002$  and  $^{208}Pb/^{206}Pb$  ratios of  
368  $2.095 \pm 0.005$  (n = 29, Table S6) that will be named Pb local ore in the following.

### 369 5.4.2 Lake sediments

370 The two deepest samples of the lake sediment core present a  $^{206}Pb/^{207}Pb$  isotopic ratio of 1.209  
371 and a  $^{208}Pb/^{206}Pb$  isotopic ratio between 2.041 and 2.042 (Fig. 4, Table S7), falling within the  
372 range of the Variscan continental crust (Monna et al., 2000). Hence, these samples may be  
373 considered as the uncontaminated local background. On a  $^{206}Pb/^{207}Pb$  vs  $^{208}Pb/^{206}Pb$  diagram,  
374 the lake sediment Pb isotopic signatures provide evidence of binary mixing between the local

375 background and the local Pb ore end-members (Fig. 4A). The proportion of anthropogenic Pb  
376 calculated from  $^{206}\text{Pb}/^{207}\text{Pb}$  ( $Pb_{\text{ANTH}}$ , equation 3) decreased from 79-84% at 80 cm depth down  
377 to 20-25% at the top of the core (Table S8). The anthropogenic Pb in the deeper samples at  
378 52 cm, 57.5 cm, 63.5 cm, and 80 cm represents more than 50% of the total Pb content (59%,  
379 66%, 79% and 84%, respectively). Such high proportions of  $Pb_{\text{ANTH}}$  are related to the highest  
380 Pb contents (e.g., at 80 cm,  $\text{Pb} = 48 \text{ mg.kg}^{-1}$ ). Even though the shallowest samples (7.3 cm,  
381 10 cm and 30.5 cm) only displayed minor enrichment from the  $EF_{\text{Pb}}$  calculation, their Pb  
382 isotope ratios display significant proportions of anthropogenic Pb, of 24%, 43% and 50%,  
383 respectively.

#### 384 5.4.3 Soils

385 The Pb isotope signature of the soil samples (Table S7) indicates a binary mixing between the  
386 local Pb-ore and the geochemical background end-members (Fig. 4), suggesting the persistent  
387 presence of anthropogenic Pb derived from local metallurgy. Samples A3, A5, B3 and B7 have  
388 isotopic signatures close to or in the range of the local background end-member (between 1.195  
389 and 1.209 for  $^{206}\text{Pb}/^{207}\text{Pb}$  and between 2.038 and 2.059 for  $^{208}\text{Pb}/^{206}\text{Pb}$ ). Samples A2, A1, B6  
390 and B1 present isotopic signatures close to the local galena (between 1.177 and 1.180 for  
391  $^{206}\text{Pb}/^{207}\text{Pb}$  and between 2.085 and 2.089 for  $^{208}\text{Pb}/^{206}\text{Pb}$ ). Samples A4, B8, B4 and B2 have an  
392 intermediate isotopic signature between the local Pb ore and the geochemical background end-  
393 members (between 1.185 and 1.189 for  $^{206}\text{Pb}/^{207}\text{Pb}$  and between 2.069 and 2.078 for  
394  $^{208}\text{Pb}/^{206}\text{Pb}$ ). Sample B5 has an isotopic signature similar to the Pb local ore. The subsurface  
395 soil samples of profile A5 and the deepest soil horizon of B6 show a more radiogenic signature  
396 ( $^{206}\text{Pb}/^{207}\text{Pb}$  ranging from 1.24-1.29) than the local geochemical background (Fig. 4). Such  
397 heterogeneity in geogenic signatures made it difficult to calculate the proportion of  
398 anthropogenic Pb in soils from the Pb isotope ratios. However, the fraction of the anthropogenic  
399 Pb was calculated from isotopic ratios using equation (3) according to the different lithologies

400 and was compared with the fraction of anthropogenic Pb calculated from the elemental method  
401 using equation (2) (Table S8; see discussion).

402 *Figure 4 should be inserted here (Pb isotopes)*

### 403 **5.5 Age-depth model of lake sediments**

404 Applying a constant flux-constant sedimentation rate (CFCS) model to an event-free  
405 sedimentary sequence (Bruel and Sabatier, 2020), the  $^{210}\text{Pb}_{\text{ex}}$  activity profile indicates two  
406 distinct periods of constant accumulation rate (AR; Fig. 5): i)  $\text{AR} = 0.99 \pm 0.3 \text{ mm.y}^{-1}$  between  
407 0 and 245 mm, and ii)  $\text{AR} = 1.25 \pm 0.2 \text{ mm.y}^{-1}$  between 245 and 335 mm. According to the  
408 computed age-depth model, the change in sedimentation rate occurred in  $1982 \pm 10 \text{ y}$ . The  
409 downcore  $^{137}\text{Cs}$  activity profile shows a first small peak at a depth of  $104 \pm 10 \text{ mm}$  and a second  
410 peak at  $290 \pm 10 \text{ mm}$ , which are associated with a peak in  $^{241}\text{Am}$  activity. The uppermost peak  
411 is attributed to the Chernobyl accident in 1986 CE and is in relatively good agreement with  
412  $^{210}\text{Pb}_{\text{ex}}$  derived ages (Fig. 5 on the right, Appleby et al., 1991). However, the  $^{210}\text{Pb}_{\text{ex}}$  derived  
413 ages are poorly equivalent to the deepest and maximum nuclear test fallout in 1963 CE,  
414 identified from both  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  activity peaks. Therefore,  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  peaks were  
415 used as privileged time-markers for the age-depth model combining  $^{14}\text{C}$  dates (Smith, 2001).

416 *Figure 5 should be inserted here ( $^{210}\text{Pb}_{\text{ex}}$   $^{137}\text{Cs}$  lake sediments)*

417 Among the 13 organic macroremains analysed for  $^{14}\text{C}$ , 4 dates were removed from the age  
418 model calculation because they were sampled at the base of event deposits and yielded ages  
419 older than the general trend (Fig. S4): Poz-121305; Poz-121306; Poz-120585 and Poz-133271  
420 (see position in Fig. S2). The Poz-133277 and Poz-144680 dates, which were the shallowest  
421 samples of the core, were also removed from the age model as they provided the oldest  
422 calibrated ages among the dated samples. Finally, only 4 dates were kept for age-depth  
423 modelling, because Poz120584, Poz133273, and Poz121164 were also too old to fit the general

424 trend of  $^{14}\text{C}$  ages and probably correspond to reworked materials (Table 2). The core depths of  
425 the Poz-144609, Poz-133272, Poz-133275 and Poz-133276 dates were computed on the master  
426 core depth (216 cm) using the correlation between cores (Fig. S2).

427 *Table 2 should be inserted here ( $^{14}\text{C}$  dates)*

428 To produce an age-depth model with radionuclides and radiocarbon ages, a smooth spline  
429 model (smoothing = 0.45, Fig. 6) was used in the clam package on event-free master core depth  
430 (155 cm; Sabatier et al., 2022). According to the age-depth model (Fig. 6), the bottom of the  
431 PLG-03 core is dated at 1581 yr cal CE at 106.8 cm ( $2\sigma$ : 1514-1640). The uncertainties ( $2\sigma$ ) of  
432 the age-depth model do not allow to properly constraint the time period of the Pb peaks  
433 (between 56.5 and 82.5 cm, Fig. 2). To improve the model accuracy around the period of  
434 interest (Fig. 6, dashed gray line), an additional historical date was implemented in the general  
435 model, which corresponds to the beginning of smelting at the Peisey-Nancroix mining site  
436 ( $1745 \pm 1$  yr cal CE, at 82 cm). These changes are visible in purple in Fig. 6 to produce a second  
437 model (in blue). According to the age-depth model, the sediment accumulation rate (SR) was  
438 relatively constant between 0 and 100 cm varying from 1.15 to 1.45  $\text{mm}\cdot\text{y}^{-1}$ . Then, it increases  
439 in depth until 150 cm to reach 2.08  $\text{mm}\cdot\text{y}^{-1}$ .

440 *Figure 6 should be inserted here*

## 441 **5.6. Anthropogenic Pb inventories**

### 442 *5.6.1 Lake sediment anthropogenic Pb inventories*

443 The accumulation rate of anthropogenic Pb ( $AR_{\text{Pb\_ANTH}}$ ) calculated on nine selected samples  
444 yielded similar results with the two methods used (elemental and isotopic; equations (2) et (3)),  
445 (Fig. 7B). In order to provide the highest resolution, the element-based ARs have been preferred.  
446 From 1593 to 1713 yr cal CE, the  $AR_{\text{Pb\_ANTH}}$  is non-significant. The oldest significant rise in

447  $AR_{Pb\_ANTH}$  is dated to 1731 CE  $\pm$  10 yr. It then peaked between 1750 and 1790, i.e. during the  
448 oldest smelting period known in Peisey-Nancroix (Fig. 7C). The most recent samples present  
449 an  $AR_{Pb\_ANTH}$  very close to pre-industrial values, even though several peaks in ARs are observed  
450 along the decreasing trend that followed the closure of the Peisey-Nancroix metallurgical site  
451 in 1824.

452 The two peaks of contamination evidenced both by the core scanner XRF data and computed  
453 ARs seem to mirror the ore production data from the local smelting site. It is characterised by  
454 two phases of activity separated by an industrial pause between 1792 and 1804 (Fig. 7C).  
455 However, the age-depth model presents large uncertainties and such an interpretation must be  
456 discussed cautiously.

457 In order to mitigate the effect of the age-model uncertainties, contaminating Pb inventories were  
458 computed over large time periods using equation (5): prior the smelting period ( $Inv_{Pb}$  prior-smelting  
459 1593-1745 yr cal CE; i.e. 152 years), during the smelting period ( $Inv_{Pb}$  smelting 1745-1824 yr cal  
460 CE; i.e. 79 years), after the smelting period ( $Inv_{Pb}$  post-smelting; 1824-2019 yr cal CE; i.e. 195  
461 years), as well as the total inventory (from 1593 to 2019 yr cal CE; i.e. 426 years). A total of  
462 19.3 g.m<sup>-2</sup> of Pb due to anthropogenic activities has been cumulated in PLG-03 core from 1593  
463 to 2019 yr cal CE; with less than 0.1% accumulated prior to the period of local smelting activity.  
464 During the 79 years of the smelting period ( $Inv_{Pb}$  smelting) a total of 7.8 g.m<sup>-2</sup> of Pb has been  
465 accumulated at the bottom of the lake, which represents a mean accumulation rate of ca. 98  
466 mg.m<sup>-2</sup>.y<sup>-1</sup>. Such inventory is comparable to that of the post-smelting period (10.7 g.m<sup>-2</sup>),  
467 although the mean accumulation rate was slightly lower during this latest period (ca. 55 mg.m<sup>-2</sup>.  
468 y<sup>-1</sup>). These inventories account for 40% and 54% of the total inventory of the core,  
469 respectively.

470 *5.6.2 Soil anthropogenic Pb inventories*

471 The anthropogenic Pb ( $Pb_{ANTH}$ ) was determined in soils using the elemental method. Thorium  
472 was used as the immobile element, as the Pb/Th ratios remained constant in the deepest soil  
473 horizons whatever their lithology. The anthropogenic contribution of Pb in soils ranges from  
474 54% to 89% of the total Pb (Fig 4). The highest percentages were found in the vicinity of the  
475 lake (A1; 86%) or within relatively flat areas higher in the catchment area (A2; 89% and B6;  
476 86%), i.e. in zones of potential accumulation. The lowest percentages were observed in A3  
477 (54%), A4 (65%), and B3 (70%), which are located in steep areas, and are thus more exposed  
478 to erosion. The inventories of anthropogenic Pb calculated from equation -6) for each  
479 superficial soil sample (20-cm thick) vary from 1.6 to 9.0 g.m<sup>-2</sup> ( $4.9 \pm 2.5$ , Table 3).

## 480 **6. Discussion**

### 481 **6.1 Recording of local ore smelting activities**

482 Lake La Plagne sediments have recorded Pb enrichments (up to  $EF = 5$ ) during the smelting  
483 period in Peisey-Nancroix (Fig. 2), between 1745 and 1824. The Pb isotopic signature of these  
484 enriched sediments is close to that of the local ore (Fig. 4). As Pb isotopes do not fractionate  
485 during ore smelting (Baron et al., 2006; Cui and Wu, 2011; Shiel et al., 2010), the observed Pb  
486 enrichment likely results from the deposition of atmospheric fallouts emitted during smelting  
487 of the Peisey-Nancroix Pb-rich ore, 7 km upwind. Such a recording of local mining activity in  
488 lake sediments is consistent with the literature (Carvalho and Schulte, 2020; Elbaz-Poulichet et  
489 al., 2020).

### 490 **6.2 Local vs regional anthropogenic Pb accumulation rates**

491 In addition to the local anthropogenic signal, lake sediments may record more regional or even  
492 global anthropogenic activities (Brännvall et al., 2001, 1999; Mariet et al., 2018). In order to  
493 investigate the importance of the regional signal, the anthropogenic Pb inventories of Lake La  
494 Plagne were compared with the anthropogenic Pb inventories of Lake Anterne, which only

495 recorded the regional signal (no local mining nor smelting activity). Lake Anterne is located 56  
496 km as the crow flies from Lake La Plagne (Massif des Aiguilles Rouges, Fig. 1B). Arnaud et  
497 al. (2004) estimated anthropogenic Pb fluxes since 1725 CE in Lake Anterne sediments,  
498 showing no significant Pb contamination prior the end of the 19<sup>th</sup> century.

499 The focus factor (equation 7) estimated from the <sup>210</sup>Pb<sub>ex</sub> inventories of Lake La Plagne and  
500 Lake Anterne allows calculating a surplus of 7.3 g.m<sup>-2</sup> of anthropogenic Pb (equation 8) for  
501 Lake La Plagne (Table 3). Lake La Plagne is therefore enriched 30 times compared to the  
502 regional signal recorded in Lake Anterne during smelting in Peisey-Nancroix (1745-1824).  
503 Such an enrichment confirms that the anthropogenic Pb recorded in Lake La Plagne results  
504 from atmospheric fallouts during smelting rather than from a more regional signal.

505 *Table 3 should be inserted here (Inventories for soil and lake)*

506 Indeed, during the period of maximum ore production in Peisey-Nancroix, the anthropogenic  
507 Pb accumulation rate (i.e., anthropogenic flux,  $AR_{Pb\_ANTH}$ ) reached  $183 \pm 67$  mg.m<sup>-2</sup>.y<sup>-1</sup>. During  
508 that period, the variations in anthropogenic Pb fluxes are consistent with the evolution of the  
509 ore production, from an average  $AR_{Pb\_ANTH}$  of 113 mg.m<sup>-2</sup>.y<sup>-1</sup> between 1745 and 1792 yr cal CE  
510 (n = 7) to an  $AR_{Pb\_ANTH}$  of 74 mg.m<sup>-2</sup>.y<sup>-1</sup> between 1804-1824 yr cal CE (n = 5, Fig. 7).

511 Anthropogenic Pb fluxes recorded at Lake La Plagne during smelting activities are high. No  
512 such high  $AR_{Pb\_ANTH}$  were recorded during the Roman, Medieval or recent times in the western  
513 Alps (Elbaz-Poulichet et al., 2020; Guédron et al., 2016; Simonneau et al., 2014; Giguët-Covex  
514 et al., 2011; Thevenon et al., 2011a, 2011b; Guyard et al., 2007; Arnaud et al., 2004). Similar  
515  $AR_{Pb\_ANTH}$  (~ 120 mg.m<sup>-2</sup>.y<sup>-1</sup>) was only recorded in a peat bog from Příbram in Czech Republic,  
516 in relation with the production of 5000 t of Pb from Pb-ore in the 19<sup>th</sup> and 20<sup>th</sup> centuries  
517 (Mihaljevič et al., 2006).

518 The total amount of anthropogenic Pb accumulated in the Lake La Plagne sediment core  
519 ( $Inv_{Pb\_anth}$ ) corresponds to a total of 19.3 g.m<sup>-2</sup>, exceeding the Pb inventories estimated from

520 various archives sampled near Pb-Ag mining districts (Bacardit et al., 2012; Yang and Rose,  
521 2005). For example, the Etang de la Gruère (Switzerland, Shotyk et al., 1998) or the Etang Mort  
522 (Spain, Hansson et al., 2017) accumulated less than  $9 \text{ g.m}^{-2}$  of anthropogenic Pb during Roman  
523 and Medieval times in peat bogs. The local industrial contamination may hence contribute to a  
524 much higher Pb load in the environment than both the global Roman and medieval  
525 contaminations.

526 Remote mountain areas have the potential to store global, regional, and local contaminations.  
527 Mountain soils have an isotopic signature ranging between anthropogenic sources driven by  
528 industrial emissions and the uncontaminated background (Lahd Geagea et al., 2008; Hernandez  
529 et al., 2003). Present-day remobilisation of past deposited leaded gasoline has also been  
530 identified as a lake contaminant (Hansson et al., 2017; Bacardit and Camarero, 2010). In this  
531 study, the Pb isotopic compositions of lake sediments and catchment soils do not show any  
532 contribution from leaded gasoline or any anthropogenic sources of Pb other than local  
533 metallurgy (Fig 4C). In lake sediments, a small Pb peak similar to the one recorded in Lake  
534 Anterne was identified in Lake La Plagne between 1965 and 1975 yr cal CE, but no Pb isotope  
535 data can confirm the presence of gasoline Pb. Lake Redò (Central Pyrenees, Spain), which is  
536 located between two mining districts (~20 km apart) operated during the last century, has  
537 evidenced no trace of gasoline Pb. However, in areas previously contaminated by smelting of  
538 nearby Pb-ore mines, the signal of Pb contamination may have been weakened due to the  
539 dilution caused by the presence of inherited Pb for several hundred years. The same seems to  
540 have occurred in Lake La Plagne. Very distant mountain catchment areas may thus have been  
541 preserved from regional Pb fluxes, showing no or minor contribution (Lake La Plagne, this  
542 study; Lake Redò, Camarero et al. 1998) in contrast to lakes located closer to urban centres  
543 (Lake Anterne, Arnaud et al. 2004, Giguet-Covex et al. 2011; Lake Lucerne, Thevenon et al.  
544 2011, Elbaz-Poulichez et al., 2020).



### 545 **6.3 Long persistence of anthropogenic Pb in lake sediments**

546 Unlike other archives, such as ombrotrophic peats that record direct atmospheric deposition,  
547 the accumulation of anthropogenic contaminants in sediments is the sum of the atmospheric  
548 deposition over the lake itself and a fraction of the deposition over the entire catchment area  
549 that has been remobilised by erosion (Bacardit and Camarero, 2010; Rose et al., 2012).  
550 Consequently, the larger the catchment and the more connected it is to the lake, the higher the  
551 contaminant inventory will be for a similar atmospheric flux.

552 During the post-smelting period,  $Inv_{Pb}$  of Lake La Plagne is 5 times higher than the  $Inv_{Pb}$  in  
553 Lake Anterne (10.5 and 2.2  $g \cdot m^{-2}$ , respectively, Table 3). A  $Surplus_{Pb}$  of 5.9  $g \cdot m^{-2}$  is hence  
554 recorded in Lake La Plagne (+56 % compared to the regional signal) during the post-smelting  
555 period (1824-1999 yr cal CE). However, the difference in  $AR_{Pb\_ANTH}$  between Lake La Plagne  
556 and Lake Anterne tends to decrease (Fig. 8A) over the most recent period (1970-1999 yr cal  
557 CE), with a local  $Surplus_{Pb}$  of 0.8  $g \cdot m^{-2}$ . These Pb inventories hence indicate a significant  
558 anthropogenic Pb surplus in Lake La Plagne since the smelter has shut down (Fig 8B). As no  
559 other source of anthropogenic Pb was identified apart from metallurgic emissions, these results  
560 suggest the presence of a pervasive source of metallurgic Pb in the catchment area due to the  
561 remobilisation of lead fallouts that had accumulated in soils during the 79 years of metallurgical  
562 activities.

563 Anthropogenic Pb remobilisation is confirmed by the Pb isotopic compositions of the  
564 shallowest sediments, which show a mixing between the local isotopic background and the local  
565 ore, with a remaining contribution of the anthropogenic Pb of 20 to 25% of the total Pb. Hence,  
566 a small proportion of the Pb emitted during smelting is still being eroded from the catchment  
567 soils nowadays and transferred to the lake. Therefore, soils within Lake La Plagne catchment  
568 area could be considered as a long-term, slowly emptying, source of anthropogenic Pb  
569 contamination. Such a process has been suggested by other studies (Yang et al., 2002, 2001).

#### 570 **6.4 Long-lasting remobilisation of legacy Pb from soil**

571 A decreasing trend in anthropogenic Pb fluxes from local inherited smelting contamination was  
572 evidenced in the sediments of Lake La Plagne, which now tends to be negligible ( $\sim 20 \text{ mg.m}^{-2}.\text{y}^{-1}$ , Fig 8A). This suggests that less and less anthropogenic Pb has been washed out from the  
573 catchment over time (Fig 8B). However, superficial soils from the catchment are not yet free  
574 of local anthropogenic Pb (Fig. 4). These combined observations suggest that the most mobile  
575 Pb has already been washed out into the lake, and that the remaining Pb might be relatively  
576 stable. Further investigations on the lead speciation should be led to confirm this hypothesis.  
577 The current inventories of anthropogenic Pb in soils seems greatly influenced by the catchment  
578 topography (Fig. 4). Indeed, the most contaminated soils are located at the footstep of the  
579 catchment area and/or on the flattest areas, where the matter eroded upstream can accumulate.  
580 In contrast, soil samples collected uphill and/or on the steepest slopes present the lowest Pb-  
581 inventories because of more intense erosion. These observations confirm the hypothesis of a  
582 progressive washing out of past lead fallouts since the end of metallurgical activities, through  
583 physical erosion processes.  
584

#### 585 **7. Conclusion**

586 This study highlights the importance of a multi-compartment approach to investigate the long-  
587 term persistence and remobilisation of anthropogenic contaminants in the critical zone. In the  
588 Lake La Plagne catchment (northern French Alps), Pb isotopes have demonstrated that Pb  
589 emitted during smelting in Peisey-Nancroix (1745-1824) fell out on the lake surface and the  
590 surrounding soils. The lake sediments have recorded this primary anthropogenic contamination,  
591 reaching  $180 \text{ mg.m}^{-2}.\text{y}^{-1}$  of Pb during the maximum production of Pb. Pb isotope ratios and  
592 estimated fluxes of anthropogenic Pb in more recent sediments provide evidence of  
593 anthropogenic Pb transfer from the catchment to the lake for the last 200 years. If such a transfer  
594 decreases over time, the catchment soils still contain a significant stock of anthropogenic Pb

595 (54-89%) that is considered as a secondary source of anthropogenic Pb dispersal into the  
596 environment. The spatial distribution of anthropogenic Pb in the catchment soils is closely  
597 linked to the topographical changes: (i) anthropogenic Pb is depleted upslope whereas it is  
598 stocked downslope by the lake, and (ii) anthropogenic Pb is accumulated on flat surfaces but is  
599 eroded in steeper slopes. Therefore, smelting that occurred 200 years ago has contributed to  
600 increasing the stock of anthropogenic Pb in both soils and lake sediments in the long-term  
601 (several centuries). Such a diffuse contamination due to atmospheric fallouts during smelting  
602 activity, the long-term persistence and remobilisation of the anthropogenic contaminants,  
603 should better be considered when investigating the mining legacy and mitigation strategies.

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## 610 **9. Appendix A – Supplementary material**

611 Supplementary material is available at the following link

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860 [https://doi.org/10.1016/S0269-7491\(01\)00107-5](https://doi.org/10.1016/S0269-7491(01)00107-5)  
861

## 862 11. Figures captions

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874 Figure 3: Distribution map of surface soils around Lake La Plagne indicating  $EF_{Pb}$ , the total  
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877 Figure 4: Pb isotope ratios of soils (surface and subsurface soils) and lake sediments compared  
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881 deepest lake sediments are considered representative of the local isotopic background (see text).  
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883 Figure 5: Age-depth model on the continuous sedimentation (events removed) based on, from  
884 left to right, <sup>210</sup>Pb<sub>ex</sub> activity (mBq.g<sup>-1</sup>), <sup>137</sup>Cs activity (mBq.g<sup>-1</sup>), <sup>241</sup>Am activity (mBq.g<sup>-1</sup>) and  
885 the age model calculated from <sup>210</sup>Pb<sub>ex</sub> on the real depth. The light grey lines represent the Ca-  
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893 3 periods: pre-smelting, smelting and post-smelting periods with <sup>206</sup>Pb/<sup>207</sup>Pb ratios of 9 samples  
894 along PLG-03; B) Accumulation rate of anthropogenic Pb ( $AR_{Pb\_ANTH}$ ) calculated using both  
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897 Figure 8: Comparison between Lake La Plagne and Lake Anterne. A) Comparison between  
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899 from  $AR_{Pb\_ANTH}$  subtracted from the regional signal (2.12 x Lake Anterne); C) Cumulated  
900  $Pb_{ANTH}$  through time in both lakes corresponding to the total inventory recorded in lakes at the  
901 sampling date.

902

## 903 12. Tables captions

904 Table 1: Principal soil properties, trace elements and major contents for superficial soils in Lake  
905 La Plagne catchment, divided in two subgroup types according to the underlying lithologies.

906 Table 2: <sup>14</sup>C dates collected in Lake La Plagne cores (PLG), with depth reported on a unique  
907 master core depth (MCD). Only 4 dates were kept for the age-depth modelling.

908 Table 3: Inventories of anthropogenic Pb and <sup>210</sup>Pb<sub>ex</sub>.

Table 1: Principal soil properties, trace elements and major contents for superficial soils in Lake La Plagne catchment, divided in two subgroup types according to the underlying lithologies.

Sample_Name	Lithology	Soil properties				Potentially toxic trace elements						Majors elements				
		pH	TOC	CaCO <sub>3</sub>	CEC	As	Cd	Cu	Pb	Sb	Zn	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO
			%	%	cmol <sup>+</sup> .kg <sup>-1</sup>	mg.kg <sup>-1</sup>						wt. %				
A2	basement rocks	4.8	6	0.05	8	27.9	0.33	15.3	133	2.36	154	53.2	13.4	5.7	2.5	1.3
A4	basement rocks	4.9	8	0.05	7	26.5	0.25	23.9	39.1	1.63	78.6	51.6	12.6	6.4	2.1	0.6
B1	basement rocks	5.1	9	0.05	14	12.2	0.29	14.3	76.3	1.84	134	49.0	11.9	5.4	2.0	1.2
B3	basement rocks	5.8	9	0.05	21	21.7	0.28	17.5	75.1	6.92	101	50.2	11.9	5.6	2.5	0.8
B4	basement rocks	4.5	6	0.20	7	17.5	0.12	17.7	96.2	4.89	107	58.3	12.2	5.9	2.4	0.1
B5	basement rocks	4.7	7	0.05	8	5.74	0.09	12.9	66.1	1.32	39.2	67.6	8.7	1.7	1.0	0.1
B6	till	5.3	7	0.05	14	6.53	0.26	23.3	102	1.29	102	60.0	10.8	5.1	1.4	0.4
A1	carbonates scree	7.3	12	0.05	31	23.8	0.43	41.2	121	3.26	103	40.9	12.5	4.9	3.2	2.5
A3	carbonates scree	6.6	11	0.05	24	37.5	0.71	20.6	51.3	1.96	99.9	44.7	12.9	3.5	4.4	1.2
B2	carbonates scree	7.2	10	0.05	31	42.6	0.39	25.6	103	3.96	151	48.1	11.3	4.6	2.6	1.5
B7	carbonates scree	7.7	6	0.90	23	22.6	0.72	15.1	101	5.58	169	49.9	13.6	6.0	4.1	1.7
B8	carbonates scree	7.5	7	5.00	18	35.6	0.33	21.9	66.9	1.99	112	42.5	10.8	4.4	6.9	7.3
A5	cargneules	5.6	10	0.05	22	16.0	1.38	19.1	116	2.08	176	43.1	12.0	5.4	3.6	0.7

Table 2: <sup>14</sup>C dates collected in Lake La Plagne cores (PLG), with depth reported on a unique master core depth (MCD). Only 4 dates were kept for the age-depth modelling.

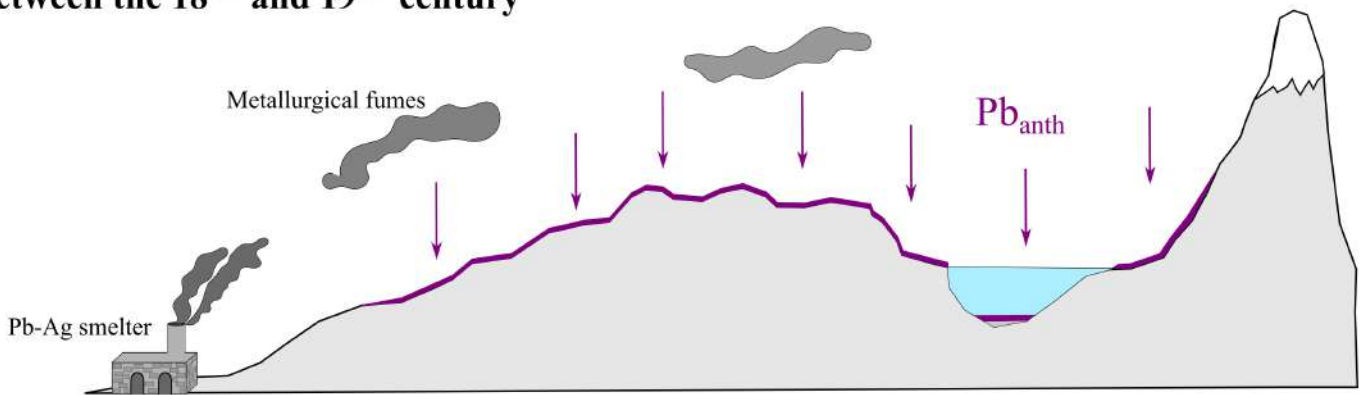
Sample Name	Core	MCD depth (in cm)	<sup>14</sup> C Ages	95% (BC/AD)
Poz-144609	PLG-04	96.3	275 ± 30 BP	1509-1795
Poz-133272	PLG-05	147.7	685 ± 30 BP	1271-1387
Poz-133275	PLG-05	178.5	740 ± 60 BP	1177-1392
Poz-133276	PLG-05	211.5	1430 ± 30 BP	585-656

Table 3 : Inventories of anthropogenic Pb and <sup>210</sup>Pb<sub>ex</sub>

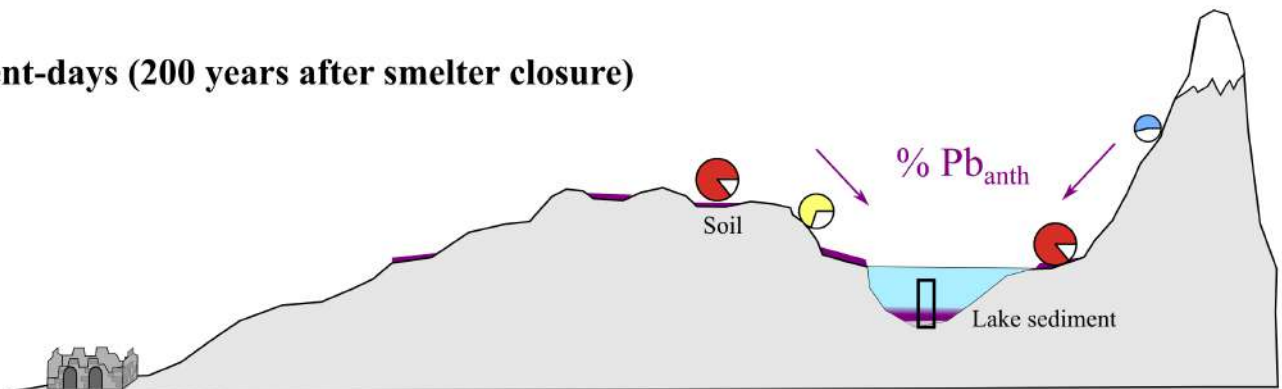
	Inv. Pb <sub>ANTH</sub> (g.m <sup>-2</sup> )				Inv. <sup>210</sup> Pb <sub>ex</sub>
	Smelting	Post-smelting	Recent	Total	Bq.m <sup>-2</sup>
Lake La Plagne sed.	7.8	8.5	1.8	19.3	17280
Lake Anterne sed.	0.3	1.9	0.4	2.5	8170
Surplus (FF = 2.12)	7.3	4.5	0.8	-	
La Plagne soils	4.88 ± 2.5 (1.64-9)				

## Graphical abstract

Between the 18<sup>th</sup> and 19<sup>th</sup> century



Present-days (200 years after smelter closure)



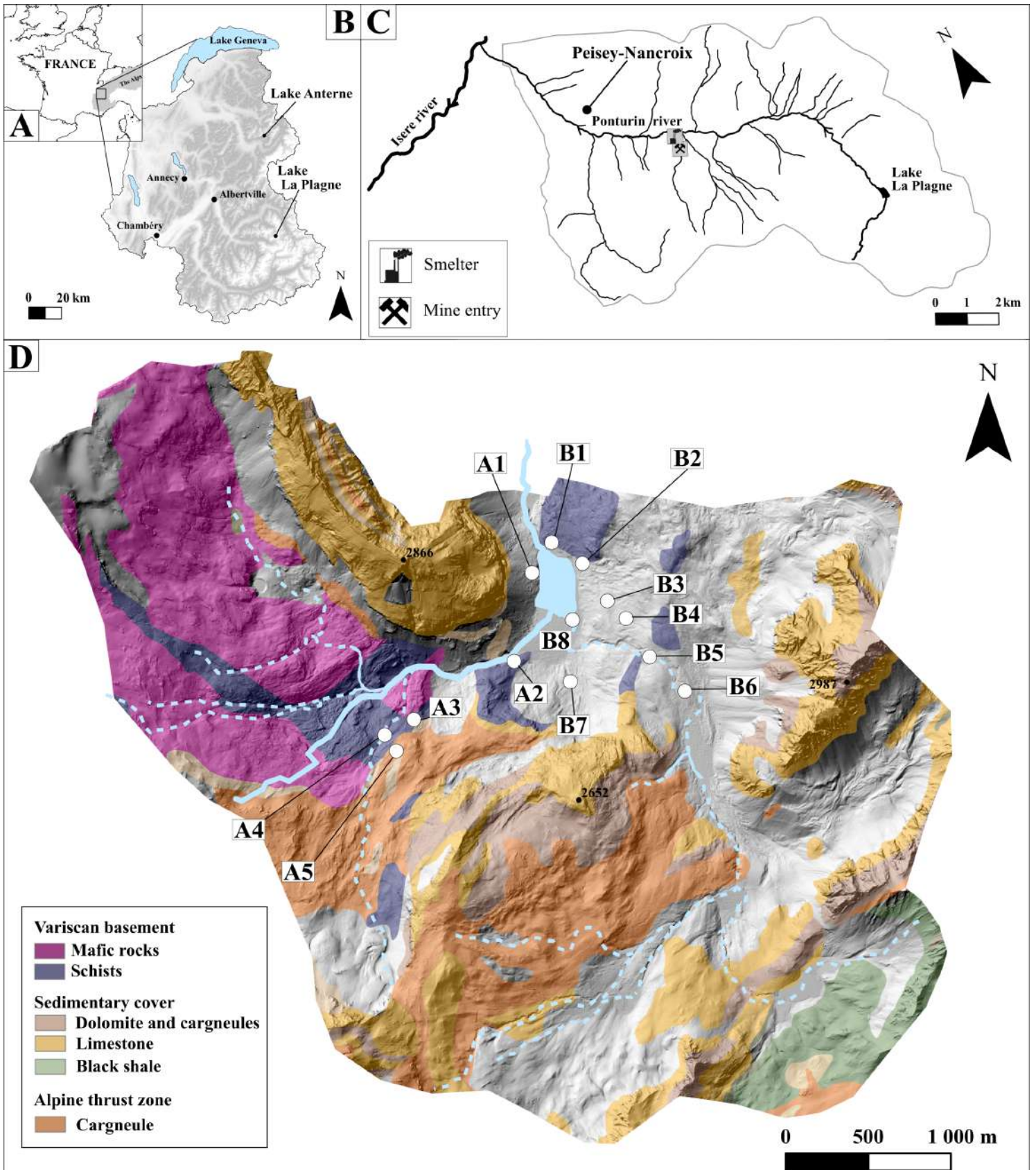


Figure 1: Location maps of the study area. A) Map of France indicating the study area; B) Location of the lakes of La Plagne and Anterne in the northern French Alps; C) Location of the Peisey-Nancroix mining and smelting areas and of Lake La Plagne along the Ponturin catchment; D) Geological map of Lake La Plagne catchment, showing the location of the soil samples.



# PLG-03

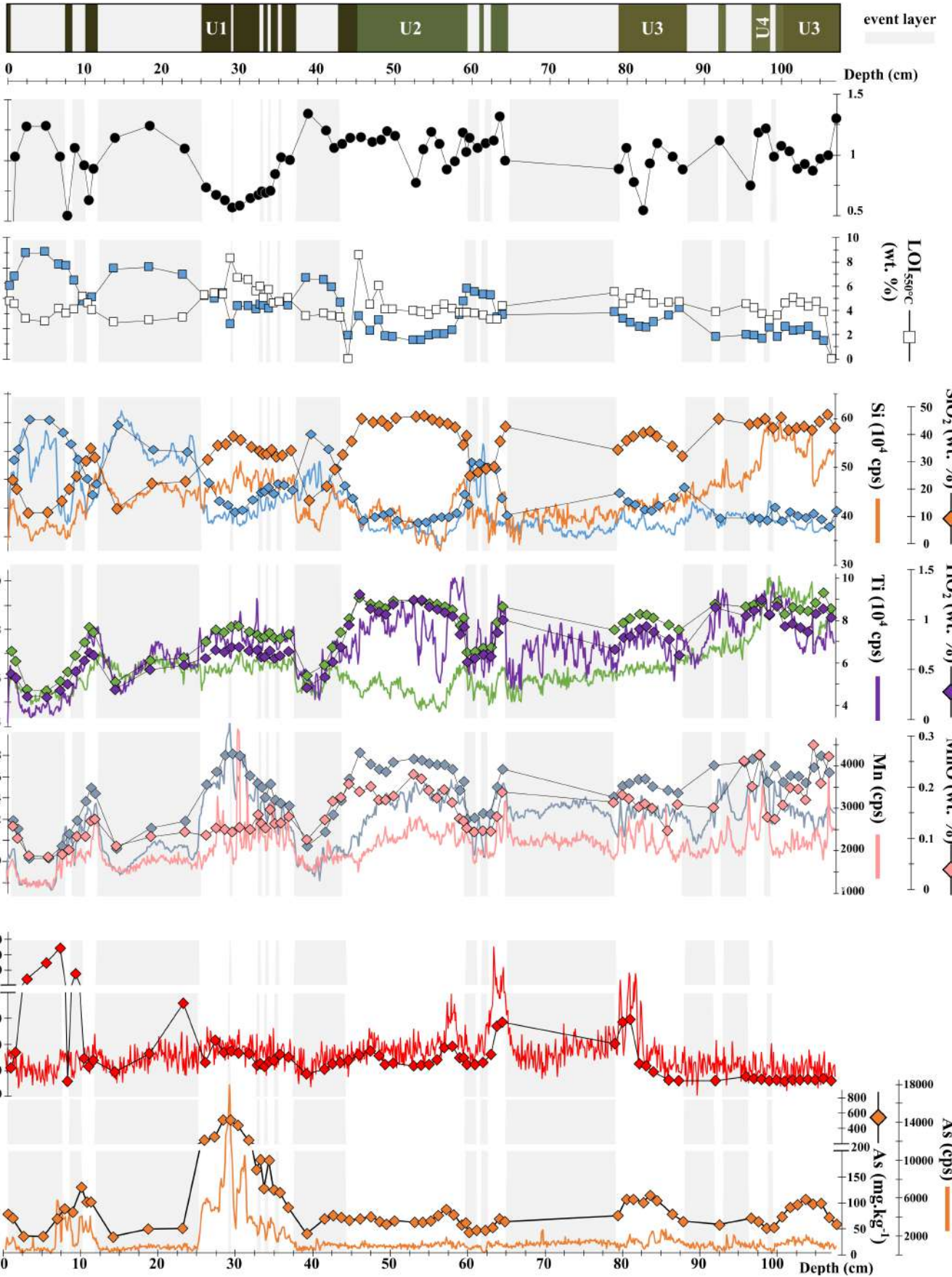


Figure 2: Dry bulk density (DBD), LOI<sub>550°C</sub> and LOI<sub>950°C</sub> (unit wt. %) and major and trace element contents measured by ICP-OES and ICP-MS (diamond, in wt. % or mg.kg<sup>-1</sup>) for discrete samples along the PLG-03 core as well as major and trace element content profiles measured by EDS-XRF with a 1-mm step (continuous line, in counts per second). Transparent grey rectangles represent the Ca-rich events and events identified during logging by a higher particle size at the base and by a different colour.

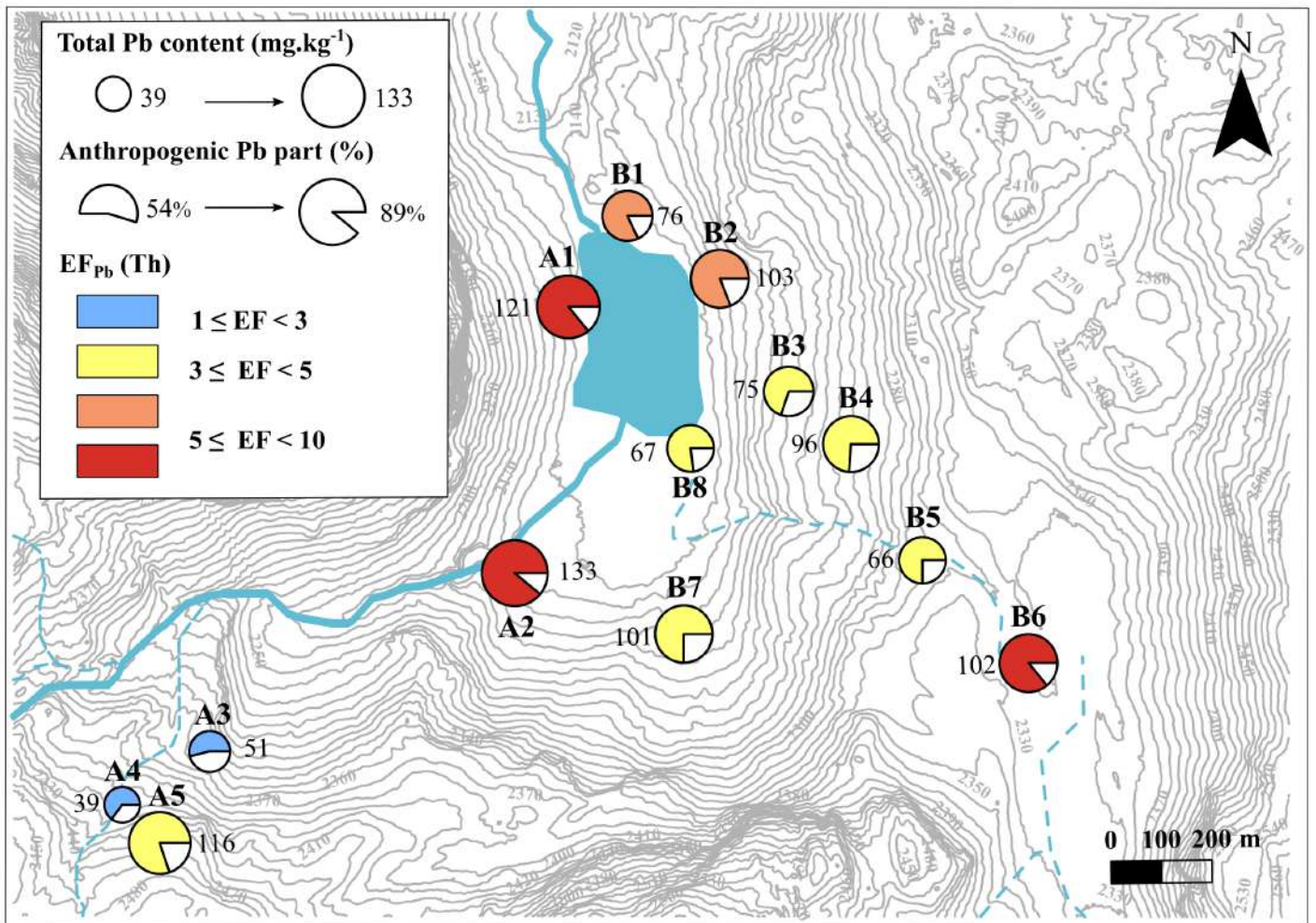


Figure 3: Distribution map of surface soils around Lake La Plagne indicating  $EF_{Pb}$ , the total Pb content (in mg.kg<sup>-1</sup>) and the anthropogenic Pb content ( $Pb_{ANTH}$  in mg.kg<sup>-1</sup>). See text for the calculation of  $Pb_{ANTH}$ .



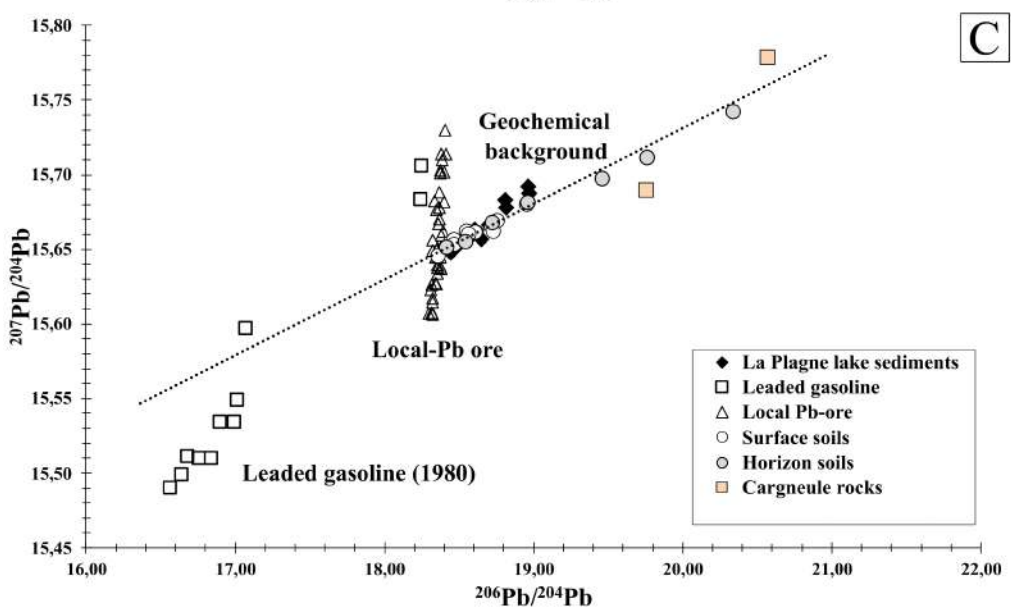
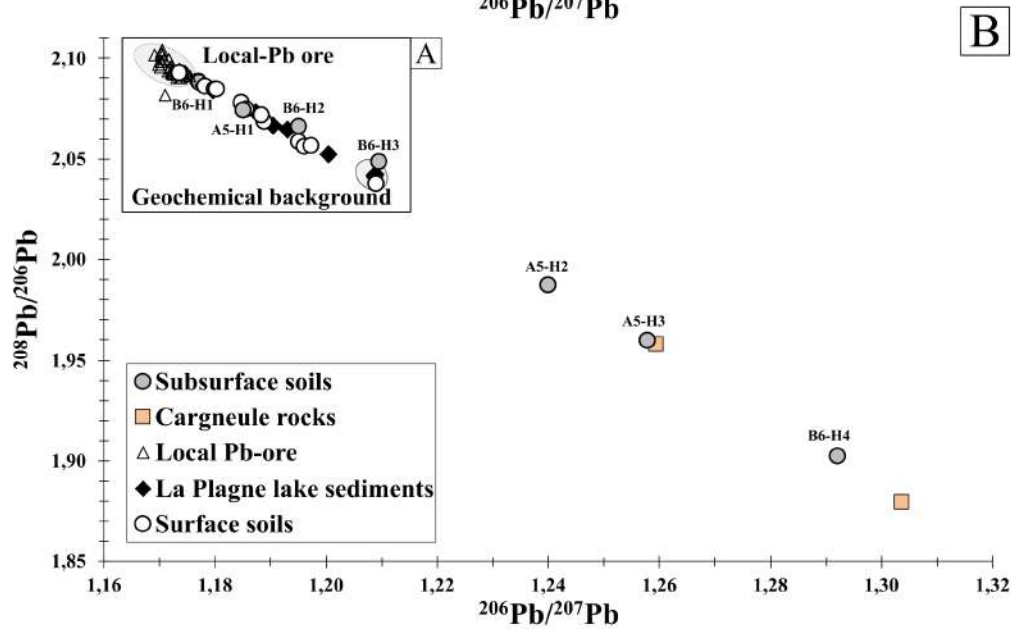
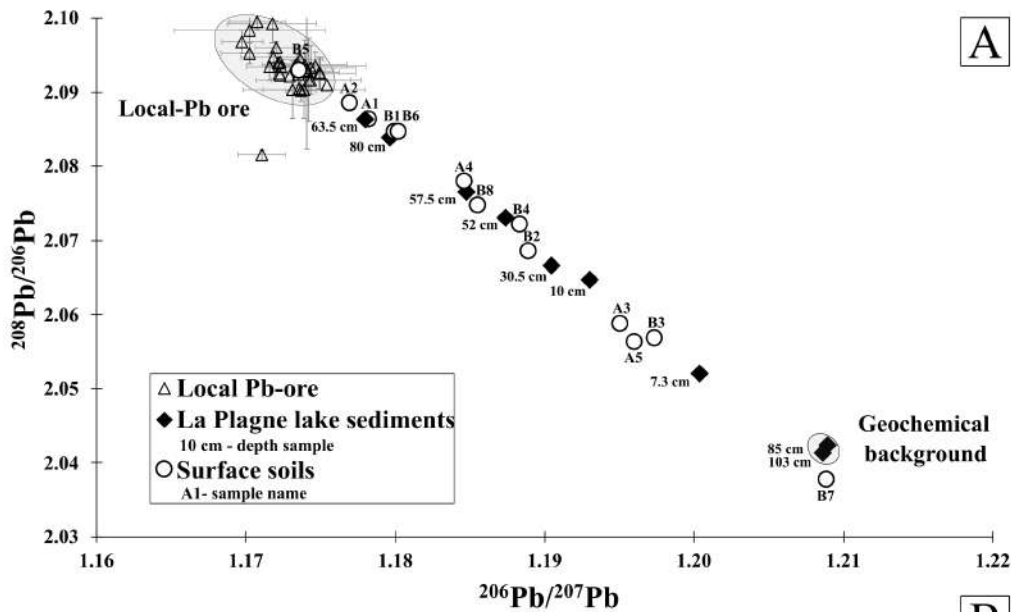


Figure 4: Pb isotope ratios of soils (surface and subsurface soils) and lake sediments compared to the local Pb ore. A)  $^{208}\text{Pb}/^{206}\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios; B)  $^{208}\text{Pb}/^{206}\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios with subsurface soils in comparison with more radiogenic cargneule rocks; C)  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios of soil and lake sediment far from leaded gasoline end-members. The deepest lake sediments are considered representative of the local isotopic background (see text). Error bars are not larger than point size for the environmental samples.

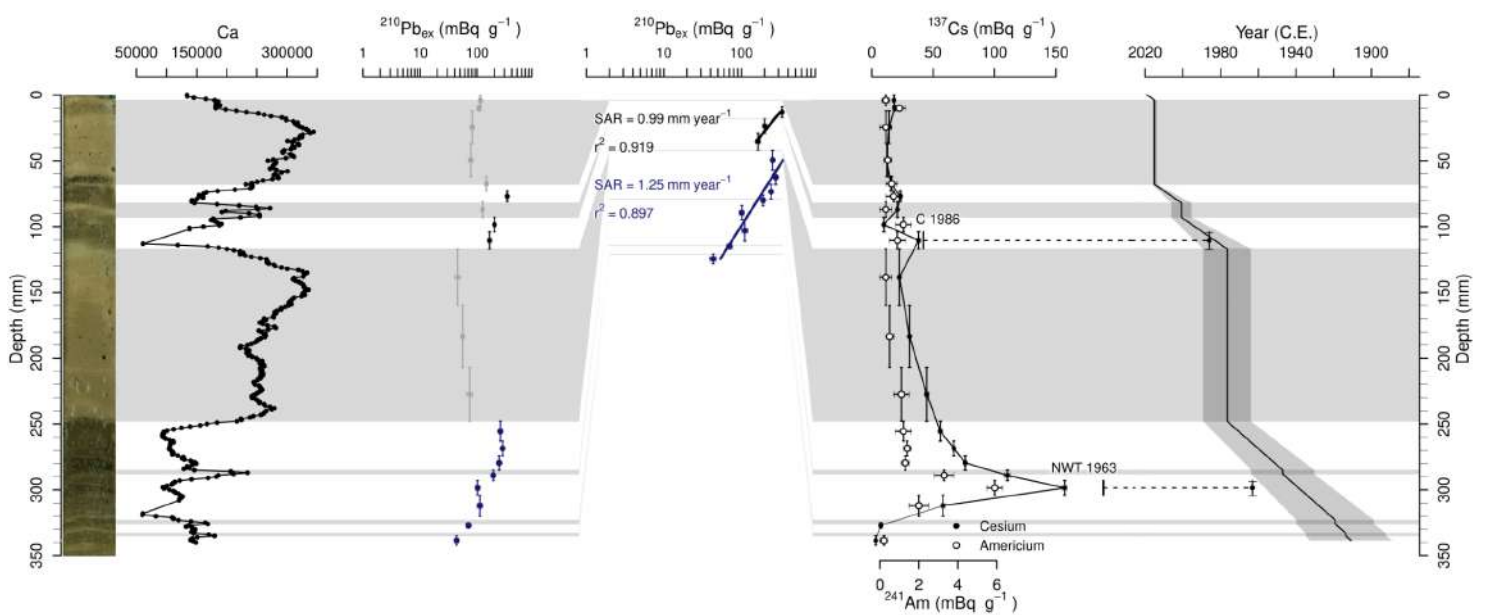


Figure 5: Age-depth model on the continuous sedimentation (event removed) based on, from left to right,  $^{210}\text{Pb}_{\text{ex}}$  activity (mBq.g $^{-1}$ ),  $^{137}\text{Cs}$  activity (mBq.g $^{-1}$ ),  $^{241}\text{Am}$  activity (mBq.g $^{-1}$ ) and the age model calculated from  $^{210}\text{Pb}_{\text{ex}}$  on the real depth. The light grey lines represent the Ca-rich events removed from the age-depth modelling. C: Chernobyl; NWT: Nuclear Weapon Test.



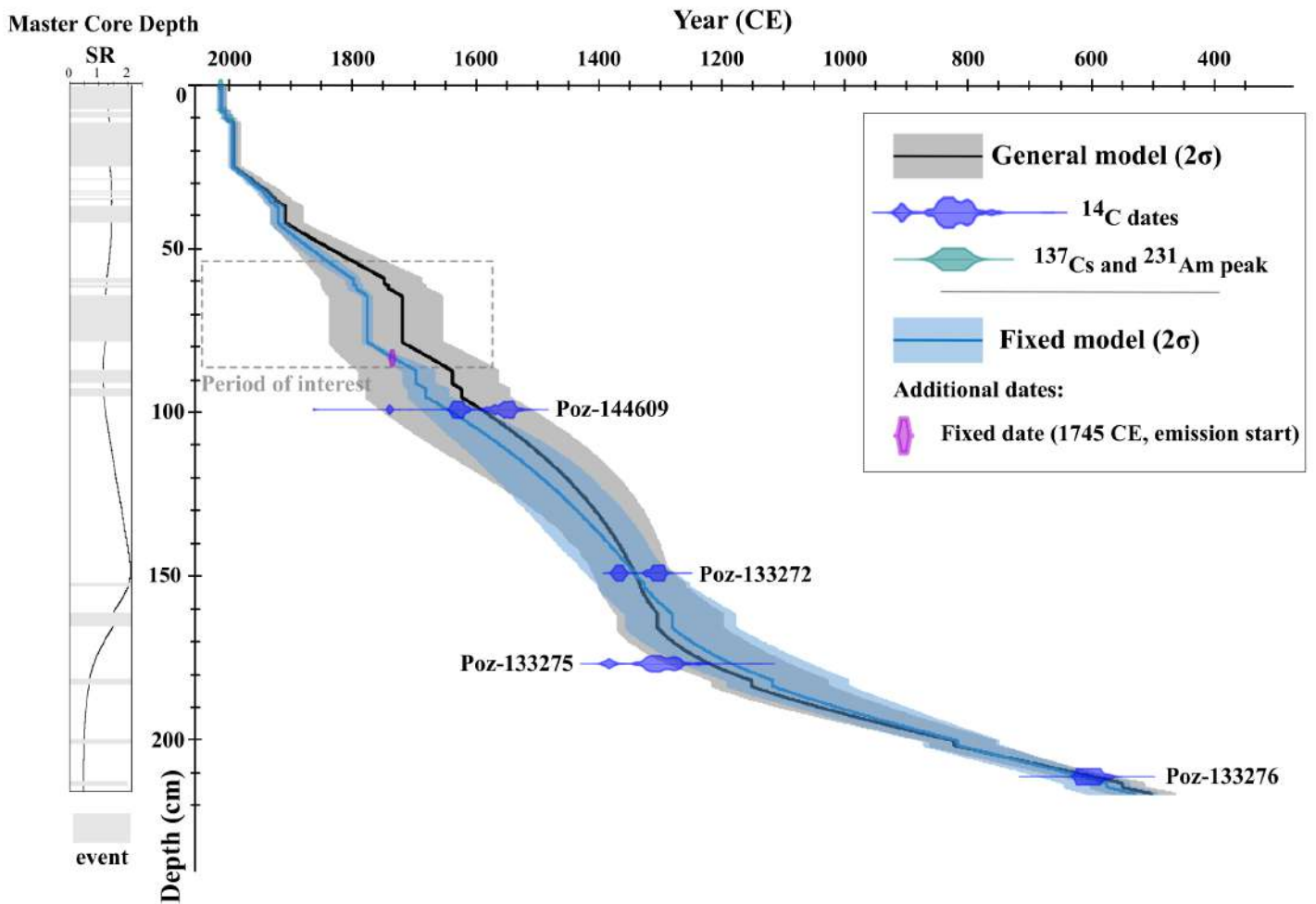


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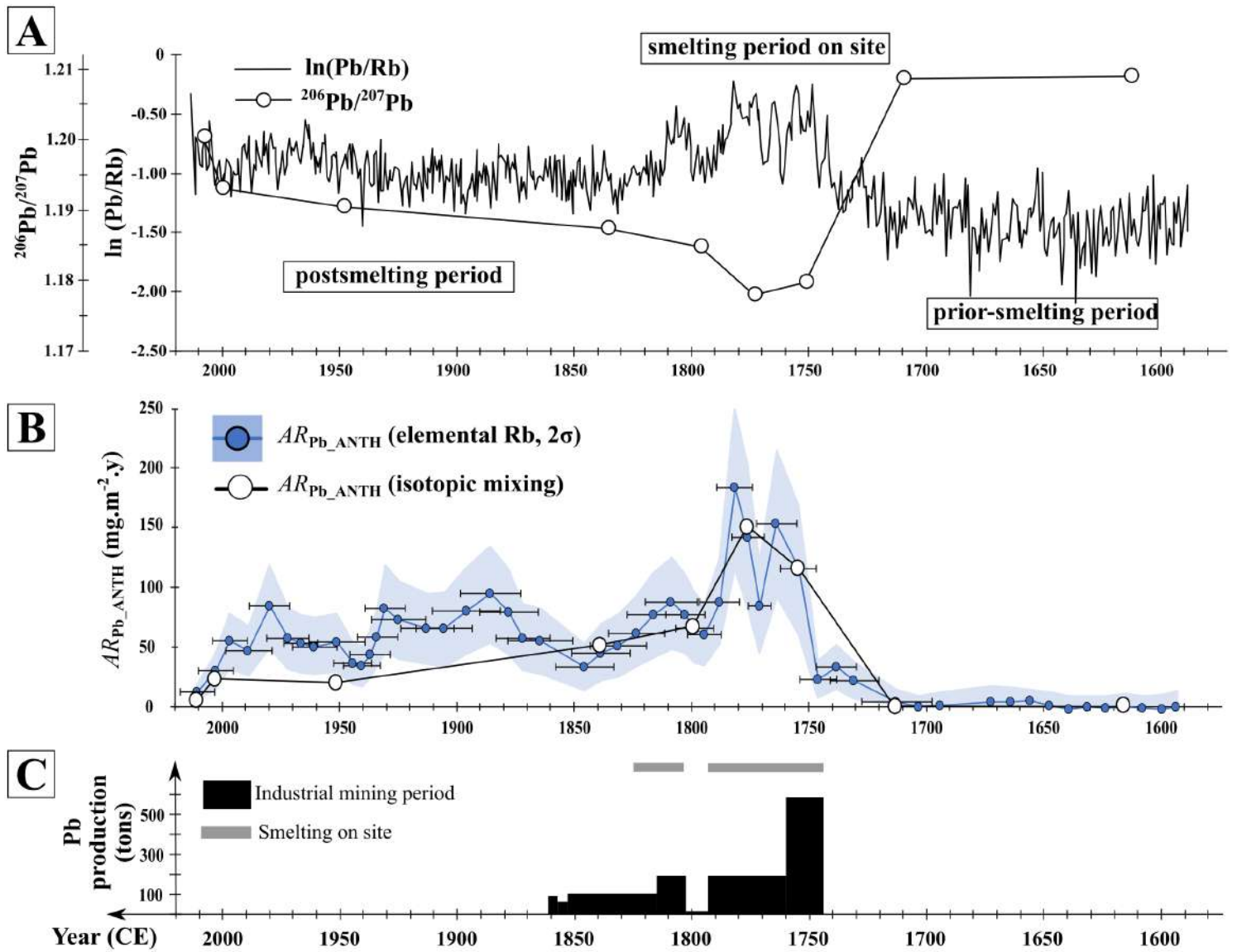


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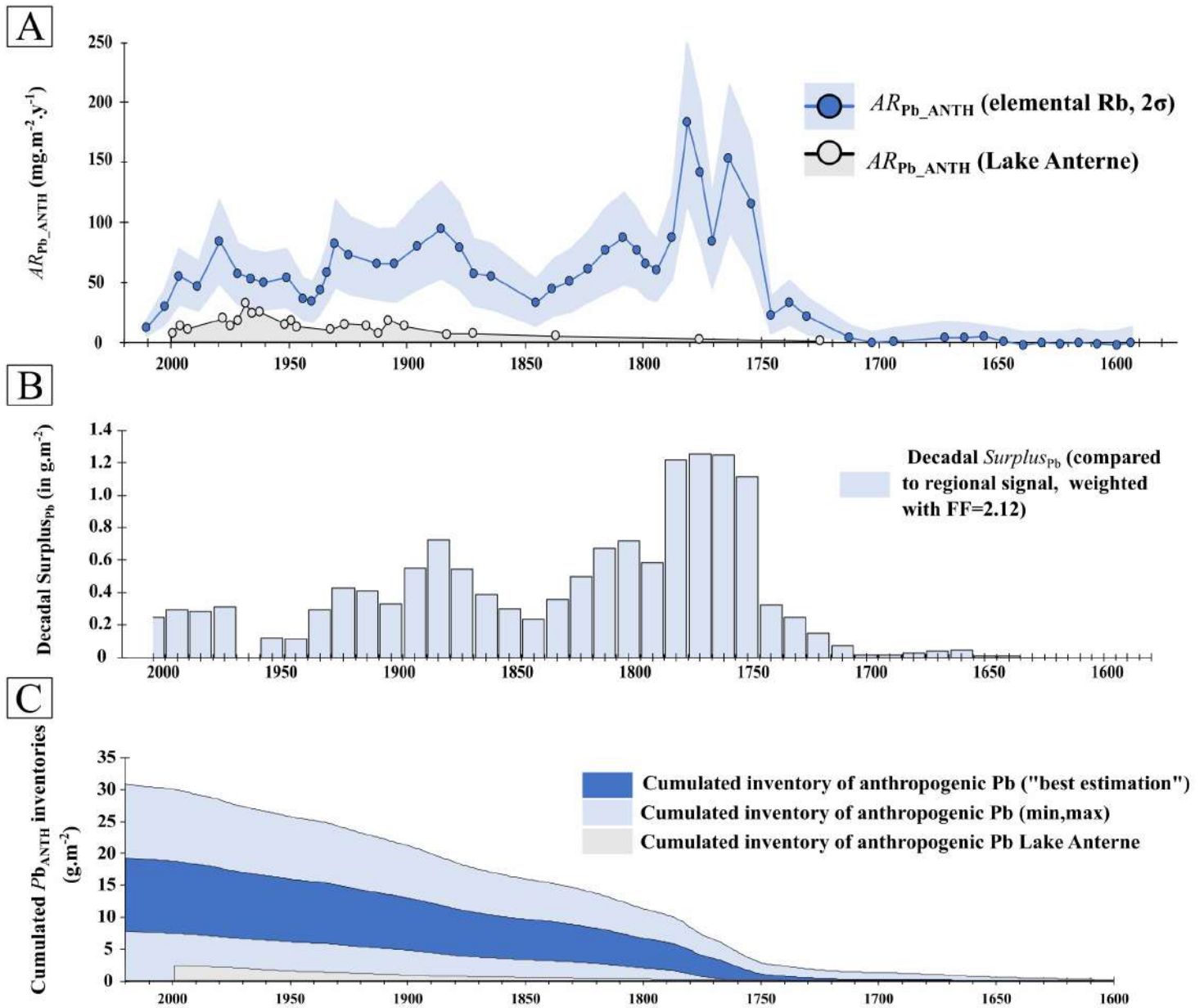


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