1  *Type of the Paper (Article)*

# High-resolution atmospheric lead pollution during the Roman period recorded in Belgian ombrotrophic peat cores

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**Abstract:** Two peat cores from two bogs were used to reconstruct high–resolution changes in atmospheric Pb accumulation rate (Pb AR) in Belgium during the Roman period. The two records were compared to assess the reliability of peat cores as archives of atmospheric Pb deposition and to established histories of atmospheric emissions from anthropogenic sources. To address these issues we analyze Pb concentration and isotopes, using ICP-MS, LA-ICP-MS and MC-ICP-MS in two peat sections, spanning 1000 yr each. Lead concentrations in the two cores range from 0.1 to 60 µg g$^{-1}$, with the maxima between 15 and 60 µg g$^{-1}$. The average natural background of Pb AR was 0.005± 0.002 mg m$^{-2}$ yr$^{-1}$ and the maximum ranges from 0.7 to 1.2 mg m$^{-2}$ yr$^{-1}$ between 50 BC and AD 215. The highest Pb AR exceed the pre-Roman period values by a factor of 25-30. Pb isotopic composition indicates that mining and metallurgical activities were the predominant sources of pollution during the Roman period. The Pb AR and chronologies in the Belgian peat cores are consistent with those reported for other continental archives as lake sediments, peat and ice cores.

**Keywords:** Atmospheric pollution, Pb accumulation rate, Peat geochemistry, Roman period, Pb isotopes

## 1. Introduction

Lead (Pb) is one of the most investigated metals in the environment, because of its high toxicity [1-4]. Anthropogenic Pb is derived from human activities such as mining, industry, coal burning and the use of leaded gasoline [e.g., 5-7]. To assess the extent of atmospheric lead contamination, it is necessary to identify the main anthropogenic and natural sources. Lead has four stable isotopes ($^{204}$Pb, $^{206}$Pb, $^{207}$Pb and $^{208}$Pb). The last three isotopes are the end-products of the natural decay chains

39    of uranium and thorium. The isotopic composition of lead ores is usually different from that of
40    bedrock [8]. Consequently, lead isotopes enable to discriminate between Pb sources of pollutants and
41    Pb derived from the erosion of the Earth crust. Lead isotopes ratios ($^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{207}$Pb) have
42    been often used as evidence of anthropogenic heavy metal pollution, particularly in peatlands [e.g.,
43    2, 5, 9-13].

44        The magnitude and timing of changes in atmospheric Pb pollution have been studied in a variety
45    of environmental archives (e.g., lake and marine sediments, ice cores? and peat) [1-2, 5, 14-15]. The
46    older indications for long-range transported (hemispheric) atmospheric pollution in Europe are from
47    3500 to 4000 years ago [16-17]. Later, during the Roman period (2000 years ago) production of silver
48    and lead was large [18] and fall-out of atmospheric emissions caused an increase of Pb atmospheric
49    pollution that was recorded in peat and lake sediments in Europe and in the Greenland ice cores [1,
50    5, 14, 17]. The Roman period shows an increase in world lead production up to 80,000 tons/year which
51    was about the same magnitude than that of the Industrial Revolution, 2000 years later [14, 18].
52    Approximately 5 % of the 80,000 tons lead production went into the atmosphere [14]. Roman
53    civilization is well known for its large-scale impact on the landscapes and environments of Europe,
54    northern Africa, and the Middle East. Lead emissions coming from mining and metallurgical
55    activities caused an important local and regional air pollution throughout Europe [e.g., 5, 19-20]. The
56    most important lead mines were situated in SW Europe (Iberia) and in SE Europe  [21]. Where, 40 %
57    of the lead production in the world was resulted from Spain, center Europe, Britain, Greece and
58    Minor Asia [21]. Then, Pb production suddenly decreased after the fall of the Roman civilization and
59    reached its minimum in the medieval ages. In the Roman period, $^{206}$Pb/$^{207}$Pb ratio values of
60    anthropogenic sources range between 1.177 and 1.185 [22].

61        Ombrotrophic peatlands can provide valuable information about the atmospheric inputs of trace
62    metals [e.g., 2, 23-26], because they are fed with nutrients and pollutants only through atmospheric
63    inputs. Most important, peat is particularly effective at preserving lead atmospheric deposition [e.g.,
64    5, 27-30]. However, due to numerous factors influencing peat geochemical content, the behavior of
65    metal elements is not always well understood despite the numerous studies carried out. The crucial
66    factor is post-depositional migration of metals. The metal elements mobility may be due to various
67    factors such as adsorption on oxy-hydroxides, variations in pH [e.g., 31-32], or uptake and recycling
68    by plants [e.g., 33-34]. Among all metals, Pb has been most often targeted for reconstruction of its
69    history of atmospheric deposition [e.g., 35]. Numerous studies demonstrated that Pb is an immobile
70    element in ombrotrophic bogs based on stable and radioactive Pb isotopes, Pb profiles in porewaters
71    comparison with rain collectors and herbarium samples and transplant experiments [e.g. 35-39].

72        Belgium as a part of *Gallia Belgica* (northern France, western Germany, southern Netherlands and
73    Belgium, Fig.1A) was occupied by the Roman Empire from 50 BC to AD 350. The Hautes Fagnes
74    Plateau (SE Belgium) has provided a key site in studies investigating human occupation and
75    environmental impact in the region since the Celtic civilization [40-44]. This area is also situated
76    southerly of Pb-Zn ore deposits (extracted since Roman period; [44-45]) and nearby the German
77    border which is 300 km from the Region of the Ruhr-Eifel industrial area. On the site several
78    archaeological [40, 44, 46-47] and historical [48] investigations support Roman occupation and ore
79    mining. Previous studies in ombrotrophic bogs from the Hautes Fagnes plateau [43, 49-51] and peaty
80    sediments [52] showed that the atmospheric pollution in Belgium dated back to early Roman times.

81  In this work, high-resolution records of Pb concentrations and stable Pb isotopic compositions in
82  two ombrothrophic peat collected from Haute Fagnes Plateau (SE Belgium) are used: 1) to track the
83  history of Pb pollution in Belgium during the Roman period; 2) to identify the Pb supplies and; 3) to
84  reconstruct the historical evolution of Pb pollution in comparison with other European archives.
85
86  **2. Materials and methods**
87  2.1. **Sampling and preparation**
88  The present study is focused on the sections covering Roman period of two ombrotrophic peats
89  located in a nationally protected peatland area, the Hautes-Fagnes Plateau in East Belgium (Fig. 1B-
90  D). The Hautes-Fagnes Plateau is part of the Stavelot Massif, mainly composed of lower Paleozoic
91  quartzites and pyllades [53]. The geological substratum is covered by post-Paleozoic sediments (clays
92  of alteration, continental and marine sands, loess – [54]) with some occasional outcrops of Early
93  Cambrian (Revinian) quartzites. Core MIS-08-01b (750 cm) was taken in February 2008 from the
94  Misten bog that is made of an accumulation of 8 m (estimated by a radar surface prospecting –[55])
95  of Holocene peat [43]. Core (CLE-15-01b, 550 cm) was taken in July 2015, from Clefaye bog, which
96  the maximum peat thickness reaches up to 5.5 m [55] and the complete peat deposit section spans
97  about 7000 years. The two ombrotrophic peats studied lie just 8 km apart.
98  The top 100 cm of the two cores was sampled by using a titanium Wardenaar corer [56]. The lower
99  peat core was cored with a Belorussian corer [57]. Since we mainly focus our study on the Roman
100 period, 60 cm from Clefaye bog (from 165 to 225 cm) and 90 cm from Misten bog (from 90 to 180)
101 which represents ~1000 yrs history (from 500 BC to AD 500) were used. Core sub-samples of 1 cm
102 thick slices were taken according to the protocol defined by Givelet et al. [58]. In Clefaye bog, the
103 sample slices were sub-sampled into three. A part of the sample slice was freeze-dried, then
104 mechanically-ground, using an agate ball mill at the University of Liège, to measure the degree of
105 humification, stables isotopes. The second part was used for geochemical analysis and the remaining
106 core samples were stored for further analyses, including dating. The Misten core was previously
107 studied by Allan et al., [2, 59-60] and Fagel et al. [61] for its chronology, atmospheric dust flux and
108 paleoenvironmental changes.
109
110 **2.2. Elemental geochemistry and Pb isotope analyses**
111 The samples from each core were analyzed separately using different methods as they were
112 initially part of two different studies.
113 **2.2.1. CLE-15-01b core (CLE)**
114 According to De Vleeschouwer et al. [62] and Boes and Fagel [63], CLE samples were subsampled
115 at 4 cm-long and 0.5 cm-thick slices and impregnated in order to consolidate them before to analyze
116 scandium (Sc), Titanium (Ti), Aluminum (Al) and Lead (Pb) concentrations. The concentrations were
117 determined by Laser Ablation Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS)
118 connected to an ESI New Wave UP-193FX Fast Excimer ArF laser of 193 nm at the Royal Museum for
119

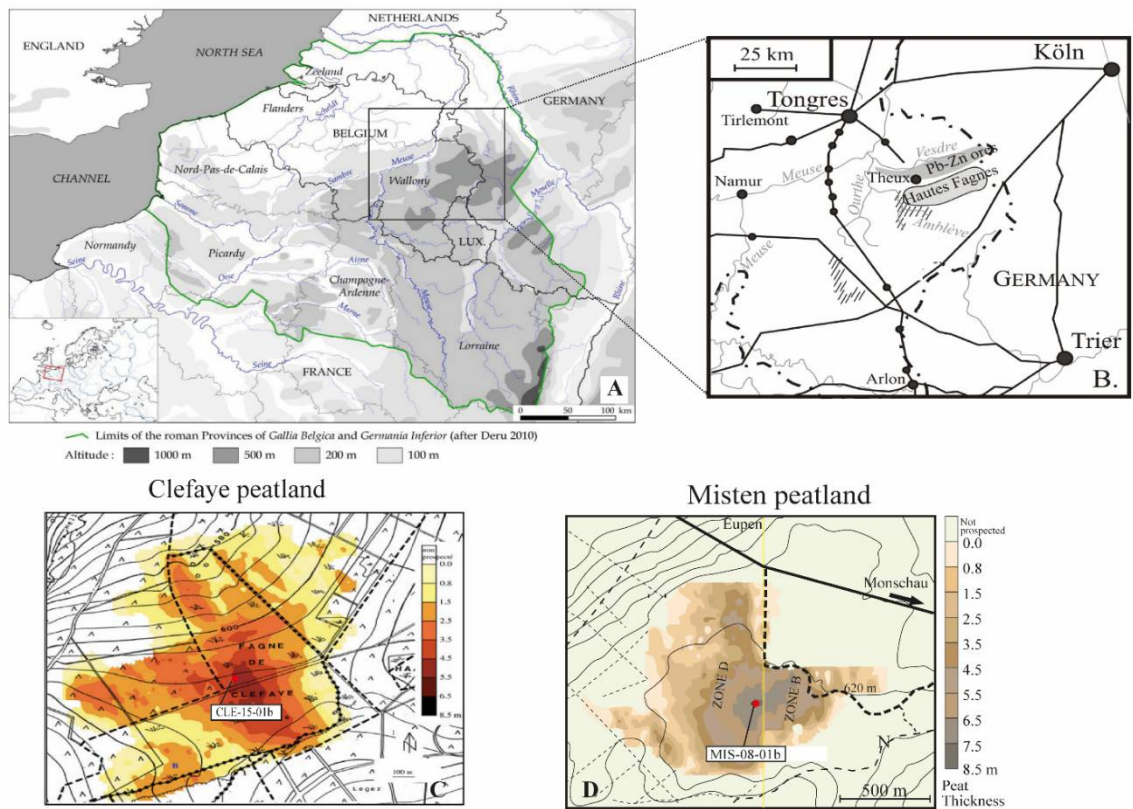



Figure 1: A. Localisation of Belgium as a part of Gallia Belgica (northern France, western Germany, southern Netherlands and Belgium)(after Deru [88]), B. Location map of the Hautes Fagnes Plateau and the Pb–Zn ores of E-Belgium (modified from De Vleeschouwer et al., [43]),   C and D. Radar derived peat thickness of the Clefaye and Misten bogs (modified after Wastiaux and Schumacker, [55]). Coring location is reported by the red circle.

Central Africa (Tervuren, Belgium). Spots were made of 50-μm diameter (spaced at 1mm intervals, samples n=595). Detection limits are calculated from the intensity and standard deviation measurements of the blank. The limits of quantification were 0.01 μg g$^{-1}$ for Sc and Pb, 1.5 μg g$^{-1}$ for Al and 0.1 μg g$^{-1}$ for Ti. Four certified plant standards (NIMT, 1547, NJV941, and NJV942) were used to assess the external analytical reproducibility. Comparison between reference values and measured values were satisfactory within ≥ 80 %.

A second aliquot was used to measure the Pb isotopic composition (Table 1). Radiogenic isotope pretreatments were carried out in a class-100 clean laboratory at ULg. About 100 mg of dried peat were placed 6 h into an oven at 550 °C to remove by combustion all organic matter (Chambers et al., 2011). After calcination, the samples were dissolved in a mixture of concentrated HNO$_3$ and HF in a proportion of 1:4 and heated at 125 °C for 48 h. The solution was evaporated to dryness and the residue was re-dissolved in 2 ml of 6M HCl to ensure complete digestion and the solutions were evaporated. For separation of Pb isotopes and REE, the samples were dissolved in 0.5 ml of 0.8M HBr and passed on Teflon column filled with AG1-X8 resin. The Pb isotopic ratios were measured using an MC-ICP-MS (Multi Collector-Inductively Coupled plasma Mass Spectrometry, Nu plasma), at the Department of Earth and Environment Sciences, (ULB, Belgium). The mass fractionation was internally corrected for mass bias using the known $^{205}$Tl/$^{203}$Tl ratio [64]. During the analysis, the Pb

144  NBS981 standard was repeatedly measured in alternation with samples in order to control any daily
145  instrument drift. The isotope ratios of the NBS981 standard were stable during the analysis session
146  [n = 47, $^{208}Pb/^{204}Pb$ =36.7052 ± 0.0094 (2s), $^{207}Pb/^{204}Pb$ = 15.4954 ±0.0031 (2s), $^{206}Pb/^{204}Pb$=16.9394 ± 0.0034
147  (2s)]. These values are consistent with the recommended values and are in agreement with the
148  laboratory long term values ($^{208}Pb/^{204}Pb$ 36.709 ± 0.021, $^{207}Pb/^{204}Pb$ 15.4951 ± 0.0066, $^{206}Pb/^{204}Pb$ 16.9392
149  ± 0.0006, n = 350).

150

151  Table 1: Pb isotope data of the CLE and MIS cores measured MC-ICP-MS. Starts correspond to
152  duplicate analyses.

| Core | Depth (cm) | 208/204 | ±2se | 207/204 | ±2se | 206/204 | ±2se | 208/206 | ±2se | 206/207 | ±2se |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CLE | 38 | 38.0280 | 0.0021 | 15.6024 | 0.0008 | 18.0447 | 0.0008 | 2.1074 | 0.00004 | 1.1565 | 0.00001 |
| | 38* | 38.0281 | 0.0020 | 15.6023 | 0.0007 | 18.0451 | 0.0009 | 2.1074 | 0.00003 | 1.1566 | 0.00001 |
| | 92 | 38.3593 | 0.0023 | 15.6218 | 0.0009 | 18.3844 | 0.0009 | 2.0866 | 0.00004 | 1.1768 | 0.00001 |
| | 92* | 38.3638 | 0.0018 | 15.6232 | 0.0006 | 18.3863 | 0.0007 | 2.0865 | 0.00004 | 1.1768 | 0.00001 |
| | 170 | 38.4082 | 0.0019 | 15.6278 | 0.0007 | 18.4104 | 0.0007 | 2.0862 | 0.00004 | 1.1781 | 0.00001 |
| | 170* | 38.4066 | 0.0018 | 15.6277 | 0.0006 | 18.4096 | 0.0007 | 2.0862 | 0.00005 | 1.1780 | 0.00001 |
| | 172 | 38.4015 | 0.0026 | 15.6263 | 0.0010 | 18.4110 | 0.0010 | 2.0858 | 0.00005 | 1.1782 | 0.00002 |
| | 174 | 38.3974 | 0.0020 | 15.6270 | 0.0007 | 18.4055 | 0.0009 | 2.0862 | 0.00004 | 1.1778 | 0.00001 |
| | 176 | 38.3866 | 0.0024 | 15.6255 | 0.0009 | 18.3991 | 0.0010 | 2.0864 | 0.00005 | 1.1775 | 0.00001 |
| | 178 | 38.3762 | 0.0019 | 15.6233 | 0.0008 | 18.3930 | 0.0009 | 2.0864 | 0.00004 | 1.1773 | 0.00001 |
| | 180 | 38.3702 | 0.0014 | 15.6216 | 0.0006 | 18.3899 | 0.0007 | 2.0865 | 0.00004 | 1.1772 | 0.00001 |
| | 182 | 38.3719 | 0.0022 | 15.6231 | 0.0010 | 18.3884 | 0.0010 | 2.0867 | 0.00004 | 1.1770 | 0.00001 |
| | 182* | 38.3729 | 0.0017 | 15.6235 | 0.0007 | 18.3891 | 0.0007 | 2.0867 | 0.00004 | 1.1770 | 0.00001 |
| | 184 | 38.3624 | 0.0021 | 15.6228 | 0.0008 | 18.3790 | 0.0008 | 2.0873 | 0.00004 | 1.1764 | 0.00001 |
| | 187 | 38.3748 | 0.0022 | 15.6234 | 0.0008 | 18.3863 | 0.0009 | 2.0872 | 0.00004 | 1.1768 | 0.00001 |
| | 189 | 38.3748 | 0.0024 | 15.6247 | 0.0008 | 18.3855 | 0.0010 | 2.0873 | 0.00004 | 1.1767 | 0.00001 |
| | 193 | 38.4329 | 0.0023 | 15.6325 | 0.0008 | 18.4032 | 0.0009 | 2.0884 | 0.00004 | 1.1772 | 0.00001 |
| | 195 | 38.4858 | 0.0015 | 15.6385 | 0.0005 | 18.4269 | 0.0007 | 2.0886 | 0.00004 | 1.1783 | 0.00001 |
| | 195* | 38.4840 | 0.0017 | 15.6381 | 0.0006 | 18.4259 | 0.0006 | 2.0886 | 0.00004 | 1.1783 | 0.00001 |
| | 197 | 38.5294 | 0.0016 | 15.6450 | 0.0006 | 18.4533 | 0.0006 | 2.0879 | 0.00004 | 1.1795 | 0.00001 |
| | 200* | 38.5306 | 0.0019 | 15.6425 | 0.0007 | 18.4681 | 0.0007 | 2.0863 | 0.00004 | 1.1806 | 0.00001 |
| | 200 | 38.5327 | 0.0016 | 15.6432 | 0.0006 | 18.4686 | 0.0006 | 2.0864 | 0.00004 | 1.1806 | 0.00001 |
| | 220 | 38.4492 | 0.0019 | 15.6384 | 0.0007 | 18.4908 | 0.0008 | 2.0794 | 0.00004 | 1.1824 | 0.00001 |
| | 412 | 38.8049 | 0.0025 | 15.6762 | 0.0009 | 18.9730 | 0.0011 | 2.0453 | 0.00005 | 1.2103 | 0.00002 |
| MIS | 69.9 | 38.48663 | 0.00186 | 15.63528 | 0.00083 | 18.50578 | 0.00092 | 2.07972 | 0.00004 | 1.18359 | 0.00001 |
| | 76.5 | 38.56519 | 0.00184 | 15.64418 | 0.00082 | 18.57075 | 0.00088 | 2.07669 | 0.00005 | 1.18708 | 0.00001 |
| | 78.7 | 38.54759 | 0.00332 | 15.63986 | 0.00141 | 18.56503 | 0.00158 | 2.07636 | 0.00004 | 1.18703 | 0.00001 |
| | 83.1 | 38.61125 | 0.00228 | 15.64727 | 0.00091 | 18.61642 | 0.00097 | 2.07407 | 0.00004 | 1.18974 | 0.00001 |
| | 88 | 38.5753 | 0.0024 | 15.6411 | 0.0009 | 18.5909 | 0.0011 | 2.0750 | 0.00005 | 1.1886 | 0.00002 |
| | 110 | 38.2657 | 0.0024 | 15.6109 | 0.0008 | 18.3112 | 0.0010 | 2.0897 | 0.00004 | 1.1730 | 0.00001 |
| | 120 | 38.3471 | 0.0018 | 15.6168 | 0.0008 | 18.3852 | 0.0009 | 2.0858 | 0.00004 | 1.1773 | 0.00001 |
| | 131 | 38.3694 | 0.0019 | 15.6239 | 0.0007 | 18.3873 | 0.0007 | 2.0867 | 0.00004 | 1.1769 | 0.00001 |
| | 134 | 38.3684 | 0.0026 | 15.6236 | 0.0009 | 18.3851 | 0.0010 | 2.0869 | 0.00004 | 1.1768 | 0.00001 |

| 135 | 38.2948 | 0.0021 | 15.6165 | 0.0008 | 18.3241 | 0.0008 | 2.0899 | 0.00004 | 1.1734 | 0.00001 |
| 138 | 38.3719 | 0.0023 | 15.6232 | 0.0009 | 18.3865 | 0.0009 | 2.0870 | 0.00004 | 1.1769 | 0.00001 |
| 146 | 38.3716 | 0.0020 | 15.6219 | 0.0008 | 18.3886 | 0.0009 | 2.0867 | 0.00004 | 1.1771 | 0.00001 |
| 170 | 38.5086 | 0.0019 | 15.6394 | 0.0008 | 18.4658 | 0.0009 | 2.0854 | 0.00005 | 1.1807 | 0.00001 |

### 2.2.1. MIS-08-01b core (MIS)

The concentrations of lithogenic and conservative elements (Sc, Ti, and Al) and trace element (Pb) were determined every 2 cm (n = 41) by HR-ICP-MS Thermo Element XR at the Observatoire Midi-Pyrénées (Toulouse, France) after complete dissolution of the 100 mg of sample with a mixture of HNO3-HF-H202 in Savillex® beakers on a hot plate in a clean room (class 100). The standards (NIMT peat, *ICHTJ*, CTA-OTL1 oriental tobacco leaves, *NIST* tomato leaves 1573 and *IAEA* lichen 336) were used to assess the external analytical reproducibility. The limits of quantification were calculated from the intensity and standard deviation measurements of 6 blanks. Comparison between reference values and measured values were satisfactory for > 90 %. The Pb isotopic data for the Roman period are from Fagel et al., [61].

### 2.3. Chronology

For both cores, radiocarbon ages (15 samples for MIS and 11 samples for CLE) were obtained on plant macrofossils extracted following the methods described in Kilian et al. [65] and Mauquoy et al. [66]. Samples were purified and graphitized prior to measurements by Acceleration Mass Spectrometry (AMS) at the GADAM Center for Excellence (University of Gliwice, Poland) following the protocol defined by Piotrowska et al. [67-68]. Activities of ^{210}Pb were indirectly determined by the measurement of its decay product [210]Po using an alpha-spectrometer (Canberra 740) according to the protocol detailed in Sikorski and Bluszcz [69] and De Vleeschouwer et al. [70]. The ^{14}C and ^{210}Pb data and the age model for core CLE are reported in Allan et al. [71], while the age model of MIS is reported in Allan et al. [59]. The Bacon age-depth software [72] was used to develop an age–depth model as well as an age range for each slice of peat. The age-depth models show that the tow cores exhibit very different growth rates, with an average value of 0.6 mm $yr^{-1}$ for CLE and 1 mm $yr^{-1}$ for MIS for the studied period (from 500 BC to AD 500).

### 3. Result and discussion

### 3.1. Density, elemental concentrations and Pb isotope ratios

In core CLE, dry bulk density ranges from 0.05 to 0.17 g $cm^{-3}$ with a mean of 0.1 g $cm^{-3}$. In core MIS, density varies from 0.03 to 0.1 g $cm^{-3}$ and average of 0.05 g $cm^{-3}$. These values vary between 0.03 and 0.05 g $cm^{-3}$ from the lower part of the core at 180-120 cm (from 500 BC to AD 120), and they increase to the upper peat section (Fig. 2).

In core CLE, the conservative elements (Al, Sc and Ti) concentrations display similar variations (Fig. 2) and are significantly correlated ($r_{Al-Sc-Ti} > 0.6$, p-values < 0.0001). The Al values vary between 2 and 300 µg $g^{-1}$ with a mean of 125 µg $g^{-1}$, from 0.01 to 0.16 µg $g^{-1}$ with a an average of 0.03 µg $g^{-1}$ for Sc, and from 0.15 to 69 µg $g^{-1}$ with a mean of 7 µg g-1 for Ti. The Pb content remain low and constant (mean< 0.2 µg $g^{-1}$) in the lower section from 225 to 200 cm (from 500 to 80 BC). Then it shows a two steps evolution with a first increase at 200–188 cm (max [Pb]= 15 µg $g^{-1}$) corresponding to the interval 80 BC-AD 100, followed by a second sharp increase at 188-181 cm (max [Pb]= 9 µg $g^{-1}$). Then Pb values decrease toward 165 cm-depth (AD 500-Fig.2).

192      In core MIS, Al, Sc and Ti concentrations display similar variations (Fig. 2) with a significant
193      correlation (r > 0.63, p-values < 0.0001). The Al values vary between 430 and 1535 µg g$^{-1}$ with a mean
194      of 770 µg g$^{-1}$. The Sc values range between 0.10 and 0.23 µg g$^{-1}$ with an average of 0.16 µg g$^{-1}$, and Ti
195      values vary from 20 to 155 µg g$^{-1}$ with a mean of 30 µg g$^{-1}$. The Pb content remains low (1-3 µg g$^{-1}$) in
196      the lower section from 180 to 160 cm (from 450 to 280 BC). Then it shows a sharp increase from 160
197      cm and reaches a maximum of 60 µg g$^{-1}$ at 132 cm (AD 85). Then the Pb content decreases toward 90
198      cm-depth (AD 490). The similarity between the Al, Sc and Ti profiles confirms that these elements are
199      not affected by any diagenetic process (immobile) and can be used to calculate the Pb enrichment
200      factor.

201      Table 1 summarizes results of Pb isotope analyses in both cores CLE and MIS. In core CLE,
202      the $^{206}$Pb/$^{207}$Pb ratio shows two main ranges: from 400 BC to 170 AD, the ratio drops from 1.182 to
203      1.764±0.00001; and from AD 200 to AD 395, the ratio increases from 1.177 to 1.780±0.00001 (Fig.2). In core
204      MIS, $^{206}$Pb/$^{207}$Pb ratio decreases from 1.180 to 1.173±0.00001 in the interval from 325 BC to AD 30, then
205      it increases to 1.188±0.00001 at AD 500.

206      **3.2.   Enrichment factor of Pb and accumulation rate (Pb AR)**

207      The variation in trace metal concentrations can be explained by changes in supply, changes in
208      their origin (natural or anthropogenic sources), differences in peat mass accumulation and the
209      quantity of mineral material in the peat. One approach to separate the influence of anthropogenic
210      sources from natural mineral material is to calculate an enrichment factor (EF$_{Pb}$) for each metal by
211      using a conservative element (e.g., Ti, Sc, Al) indicative of the mineral material amount. In this study,
212      the Sc values were used to calculate EF$_{Pb}$ as follows [73]:

213

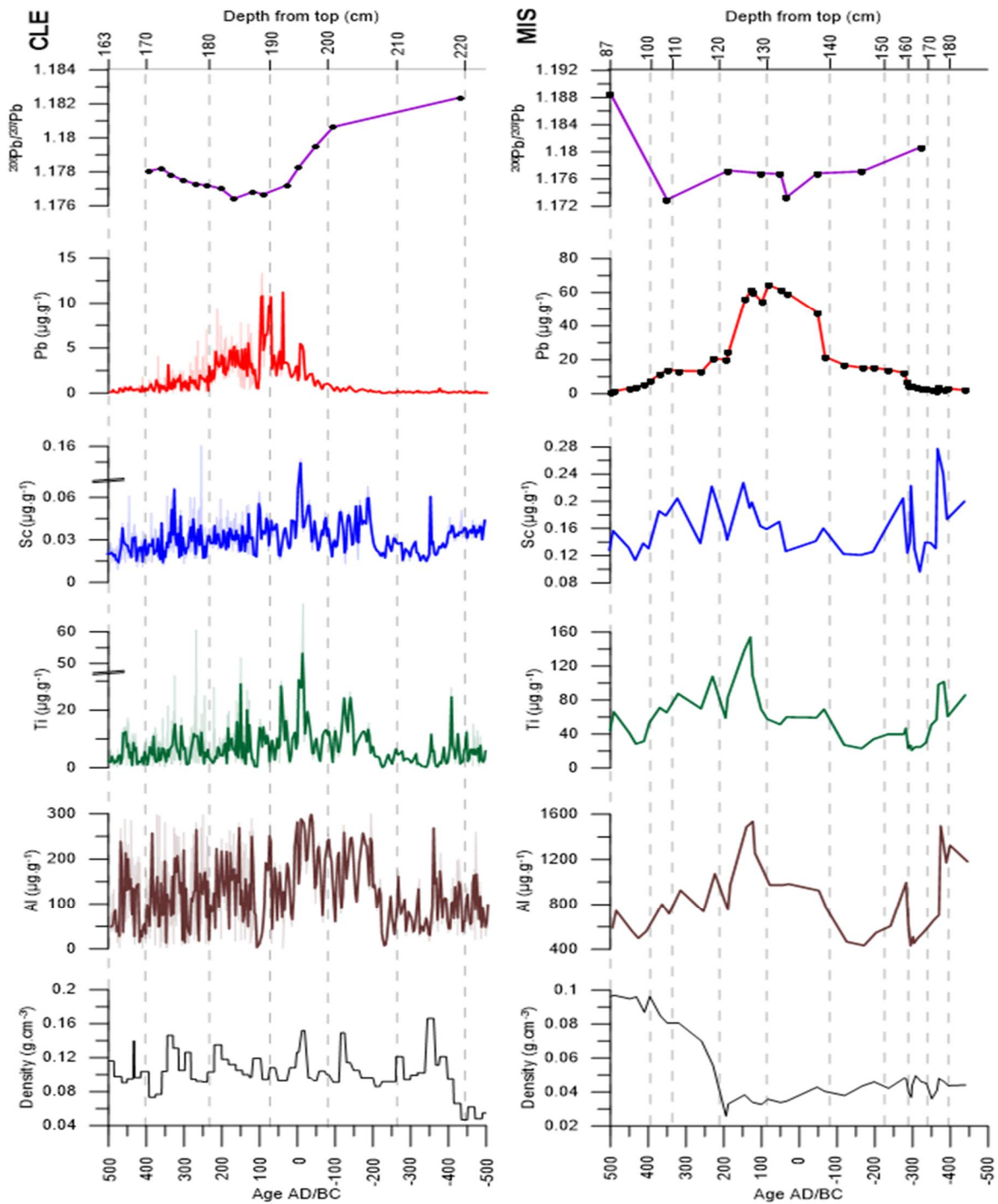
214      $EF_{Pb} = ([Pb]/[Sc])_{peat} / ([Pb]/[Sc])_{local}$         (1)

215

216      where ([Pb], ([Sc])$_{Peat}$ is the total concentration of Pb and Sc measured in the peat samples, ([Pb],
217      [Sc])$_{local}$ is the abundance measured at the bottom section of the peat, by averaging the value of 45
218      samples taken from 600 to 750 cm in MIS core and the value of 250 samples taken from 450 to 535 cm
219      in CLE core, representing the natural pre-anthropic elemental background (Allan, unpublished data).

220      In the core CLE, EF$_{Pb}$ values vary from 0.5 to 115 and from 2 to 105 for the core MIS (Fig.3). In both
221      cores EF$_{Pb}$ values remain low from 500 to 200 BC and increase to reach a maximum between AD 50
222      and AD 225 for CLE and between 60 BC and AD 200 for MIS. Finally, EF$_{Pb}$ values decrease toward
223      the upper section of cores. The location and assigned chronology of the maximum EF$_{Pb}$ differ in each
224      core. Nevertheless, the increase in EF$_{Pb}$ values in each core is coincident with the period of Roman
225      mining activities.

226

227

228   Figure 2: Evolution of density, elemental concentrations (Al, Ti, Sc and Pb), and radiogenic isotope

229   $^{207}Pb/^{206}Pb$ ratios versus age and depth in CLE and MIS cores.

230

231       The use of trace element accumulation rates (AR) instead of concentrations or enrichment factors

232   is more appropriate, as variations in net peat accumulation and decomposition are taken into account.

233   The peat accumulation rate varies within a profile and differences between cores profiles can be

234   caused by differences in surface growth rates and in decomposition rates because peat compaction

235   increases with decomposition. Based on age-depth model, density and [Pb], the Pb accumulation rate

236   can be calculated as follow:

237

238      Pb AR (mg m$^{-2}$ yr$^{-1}$) = [Pb] (μg g$^{-1}$) *density (g cm$^{-3}$)*accumulation rate (cm yr $^{-1}$)*10      (2)

239

240      Pre-Roman period Pb AR was measured from 500 to 100 BC (Pb AR=0.1 mg m$^{-2}$ yr$^{-1}$ for CLE and Pb

241      AR=0.4 mg m$^{-2}$ yr$^{-1}$ for MIS). In core CLE, the Pb AR remains lower than 0.15 mg m$^{-2}$ yr$^{-1}$ from 500 to

242      80 BC (Fig.3), then it increases from the inception of the Roman period at 50 BC to reach a maximum

243      of more than 0.7 mg m$^{-2}$ yr$^{-1}$ between AD 70 and AD 215. Then Pb AR decreases to less than 0.02 mg

244      m$^{-2}$ yr$^{-1}$ at the end of Roman period. In core MIS, the Pb AR remains lower than 0.4 mg m$^{-2}$ yr$^{-1}$ from

245      450 to 80 BC (Fig.3). Then Pb AR increases to reach a maximum of more than 1.2 mg m$^{-2}$ yr$^{-1}$ between

246      50 BC and AD 150. Since then the Pb AR decreases to less than 0.3 mg m$^{-2}$ yr$^{-1}$ at the end of Roman

247      period (i.e., after AD 350). During the Roman period, the maxima Pb AR are characterized by values

248      higher than 25-30 times the natural background values (< 0.03 mg m$^{-2}$ yr$^{-1}$ in CLE and < 0.07 mg m$^{-2}$

249      yr$^{-1}$ in MIS).

250      An intra-site variability in Pb AR values is observed when CLE and MIS cores are compared.

251      During both the pre-Roman and Roman periods Pb AR at MIS is higher than at CLE. However, they

252      both indicate similar chronologies of the Pb AR. As the two bogs are influenced by similar climate

253      regime (nearby bogs located ca. 8 km of distance and similar altitudes), an actual difference in Pb AR

254      values at the two sites is unlikely. Such difference may be explained by the within-bog spatial

255      heterogeneity and/or the Pb measurement resolution. The difference between hummocks and

256      hollows is well established, where hummocks are known to have higher interception of atmospheric

257      particles [2]. Indeed, the MIS core was taken from a hummock and CLE was taken between a

258      hummock and a hollow. Therefore, MIS may have better trapped atmospherically deposited Pb than

259      the CLE bog due to a favorable micro-topography. The Pb concentrations were measured in the core

260      CLE by LA-ICP-MS with a resolution of 1 mm and by ICP-MS in the core MIS with a lower resolution

261      of 2 cm. This suggests that particle deposition has been affected by the micro-topography in this

262      study.

263      The mean natural background of Pb AR (before 500 BC, 0.005 ± 0.002 mg m$^{-2}$ y$^{-1}$-; unpublished

264      data) for CLE and MIS is similar to published values of 0.007 ± 0.002 mg m$^{-2}$ y$^{-1}$ from 2000 BC to 900

265      BC for an England peat [1], 0.01±0.003 mg m$^{-2}$ y$^{-1}$ obtained from 5000 to 3000 BC for a Swiss peat [5].

266      Such comparison suggests that Pb AR values in CLE and MIS cores before 500 BC correspond to

267      deposition of geogenic Pb. The dramatic increase in Pb AR recorded in CLE and MIS cores (from 50

268      BC to AD 200) is in good agreement with other studies on European peats which show a peak due to

269      Roman Pb mining [1, 5, 13]. The maxima Pb AR in the CLE and MIS peat cores are within the range

270      0.7-1.8 mg m$^{-2}$ y$^{-1}$ (50 BC-AD 200): such values are 25-30 times the natural background values. This is

271      in good agreement with the maximum values recorded in Spanish peat bogs (0.3-0.9 mg m$^{-2}$ y$^{-1}$) which

272      are 10-30 times the background values (0.025-0.031±0.015 mg m$^{-2}$ y$^{-1}$) from 550 BC to AD 500 [13, 25 ].

273      In a Swiss peat bog core, the maximum Pb AR is 37 times the background value for the Roman period

274      [5]. Le Roux et al., [1] also showed that the maximum Pb AR value (0.22 mg m$^{-2}$ y$^{-1}$) during the Roman

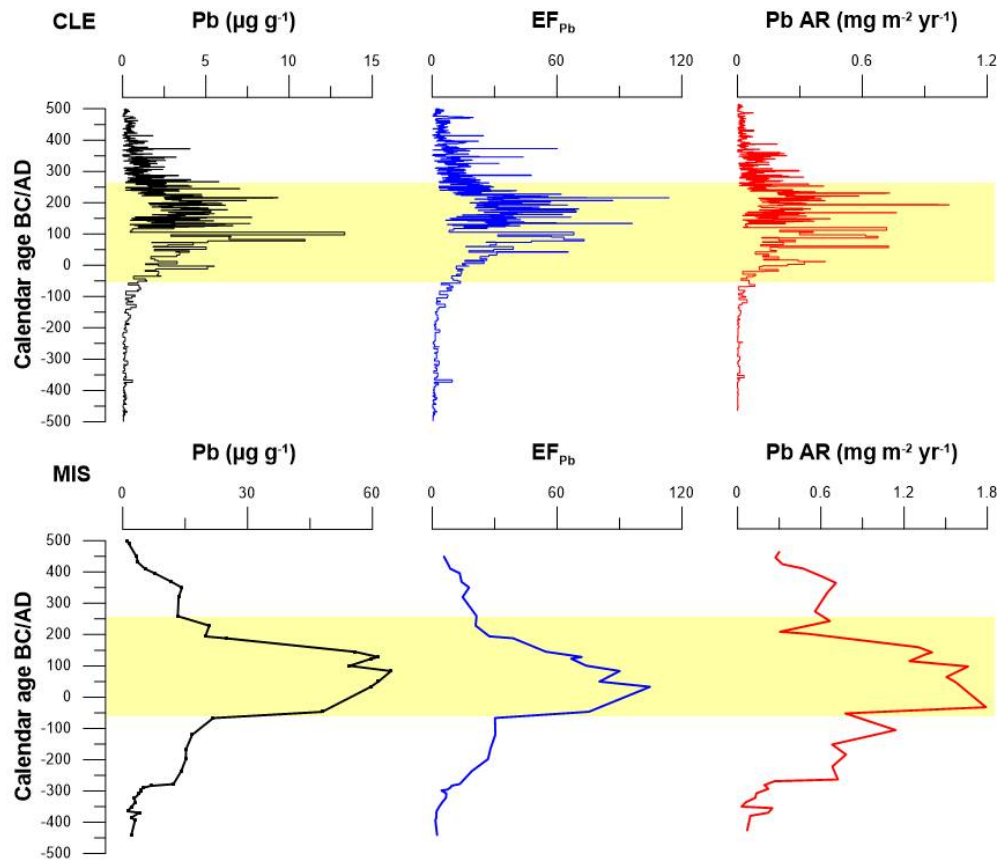
275      period was 34 times higher than that of the pre-Roman period. In peat bogs cores from southern Black

276      forest-SW Germany, Le Roux et al. [38] showed that the Pb AR is more than 40 times the background

277      values (0.02-0.03±0.01 mg m$^{-2}$ y$^{-1}$). We can conclude that the Pb AR and chronologies in the CLE and

278      MIS cores are consistent with those reported for other European peat records. The increase Pb AR

279      obtained from the two cores is a valid indication of an increase of the atmospheric pollution during

280      the Roman period.

282 Figure 3: Summary of Pb concentration, $EF_{Pb}$, and calculated Pb AR (in mg m$^{-2}$ yr$^{-1}$) for CLE and MIS
283 cores. Yellow zone corresponds to zenith Roman Empire.

### 3.3. Identification of Pb sources

286     Roman mining and metallurgical activities all over NW-SW Europe and around the
287 Mediterranean Sea increased significantly the amount of atmospheric Pb [e.g., 5, 15, 20, 61, 74 61].
288 The Pb isotope ratios deposited in CLE and MIS peat cores vary from 1.729 to 1.178 for $^{206}Pb/^{207}Pb$
289 ratios and from 2.086 to 2.089 for $^{208}Pb/^{206}Pb$ ratios (Fig.4).
290     In order to identify the source of lead, our Pb isotope data are compared with Belgian ores and
291 Pb–Zn ores from the Verviers syncline exploited during the Roman period [75-76], Germany ores
292 [77], Benelux modern aerosols [78], the Belgian pre-industrial background [43- This study] and the
293 Upper Continental Crust [79]. In the binary diagram $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$, most of the CLE and
294 MIS core data plot in the isotope field defined by Belgian ores [75-76], Eifel ores [77], Pb–Zn ores from
295 the Verviers syncline [75-76] (Fig.4). The Pb isotope ratios measured in CLE and MIS samples for the
296 Roman period between 40 BC and AD 300 correspond to the isotopic fields of the Pb-Zn ores of the
297 Verviers syncline, Belgian ores and the Eifel ores [77]. Most samples from the post/pre-Roman period
298 have mixed Pb isotopic signatures between those of Belgian ores and that of the Belgian pre-industrial
299 background. Note our results are consistent with those obtained by De Vleeschouwer et al. [43] in a
300 former core recovered in the Misten bog and by Renson et al. [44] from peat columns (RC1) in the
301 Hautes Fagnes Plateau (Fig. 4). The Pb isotopic ratios of this study show that the Clefaye and Misten
302 peats are influenced by a mixture of local and regional anthropogenic sources.

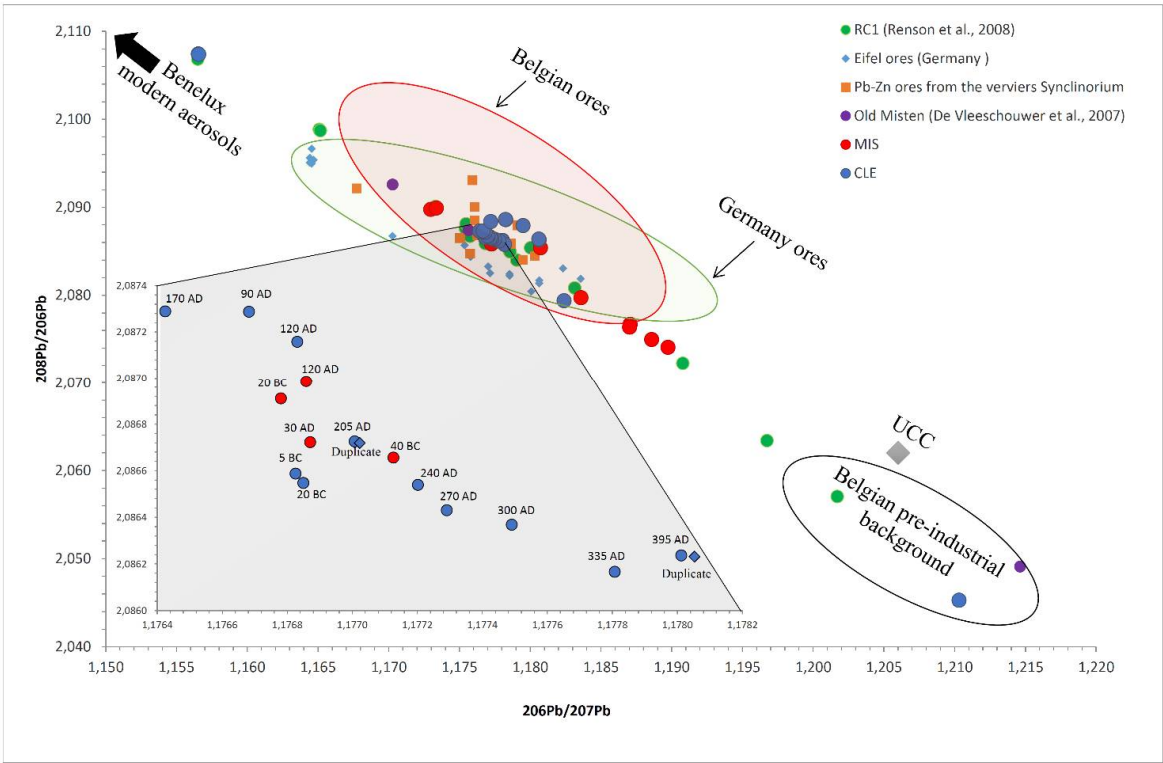



Figure 4: Binary diagram $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$. Benelux modern from Bollhöfer and Rosman [78]. Belgian ores and Pb-Zn ores from the Verviers Synclinorium from Cauet and Herbosh [75] and Dejonghe [76]. German ores from Durali-Mueller et al., [77]. Belgian pre-industrial background from this study and De Vleeschouwer et al., [43] and upper continental crust from Millot et al., [79].

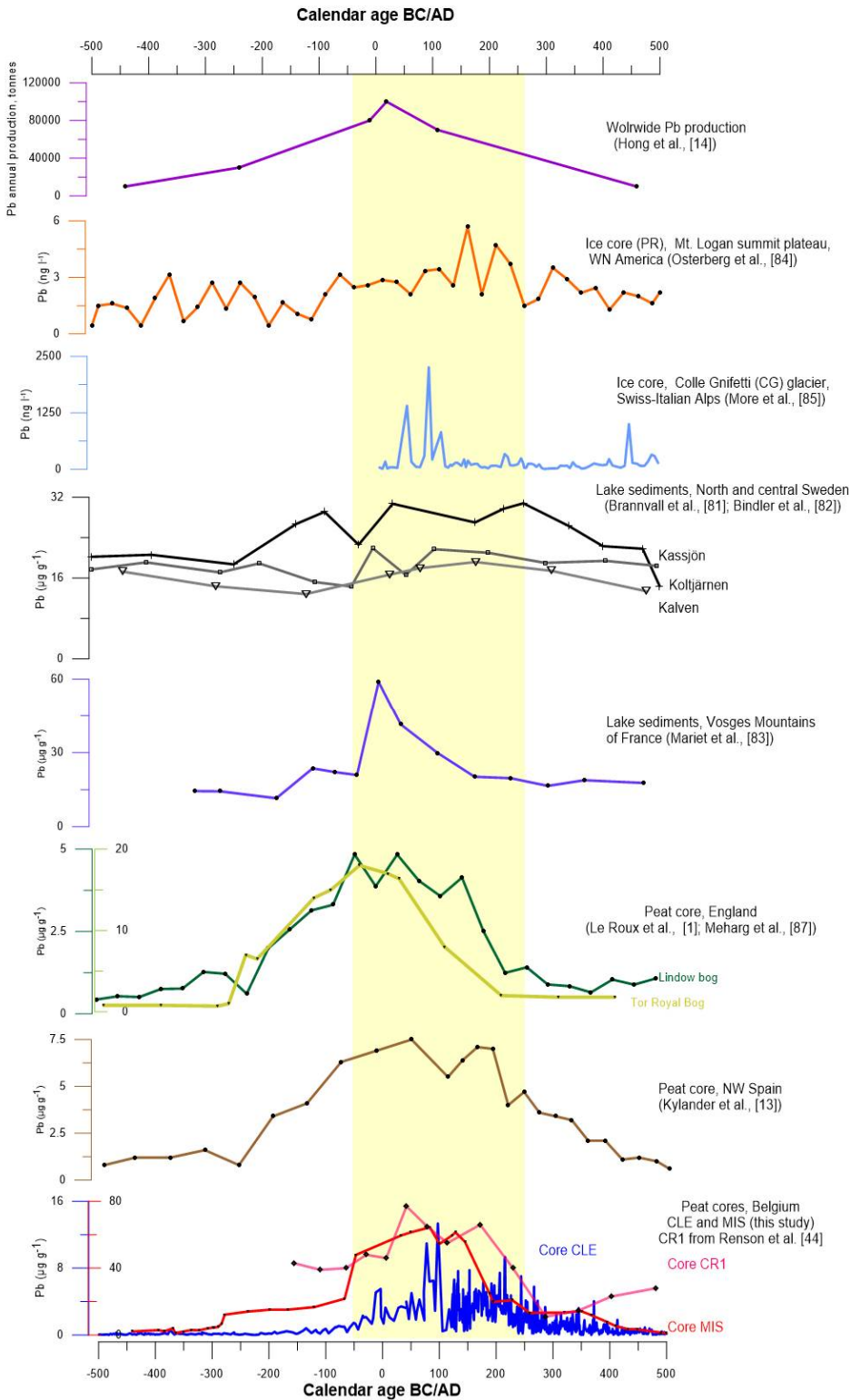
### 3.4.   Temporal evolution of Pb contamination

The increased atmospheric lead deposition in the Belgian peat records displays significant variability during the Roman period, with maxima observed between 80 BC and AD 230 (Fig. 5). At least six local maxima are identifiable, centered at ~50 BC, AD 5, ~ AD 75, ~AD 130, ~AD 180, and ~AD 215, pointing to changes in the intensity of mining and metallurgy activities in the area. This pattern is also followed by higher Pb enrichment factors (Fig.3) in parallel with a decrease in the $^{206}Pb/^{207}Pb$ ratio (Fig.2). The inception and end of Pb contamination period reflects the rise and subsequent fall of the Roman Empire in West Europe, reinforcing the validity of the age-depth model.

The Pb concentrations from Belgian peat records increase since ca. 200 BC to reach a maximum at ~ 50 BC (Fig.5), coinciding with the period of Late Iron Age and Early Roman Empire, related to Celtic mining activity [40, 42]. The Celtic people established in South Belgium from 480 BC to 27 BC and developed gold extraction from river sediments and arkose mines [40, 42, 46]. The gold mining activity are attested by more than thousand archeological sites in Southeast Belgium [46]. Between AD 75 and AD 230, corresponding to the zenith of the Roman Empire, the Pb concentrations increase to a maximum > 15 µg g-1 for CLE and > 60 µg g-1 for MIS (fig.5). During this period, Pb AR and EF$_{Pb}$ are higher and $^{206}Pb/^{207}Pb$ ratios show lower radiogenic values ($^{206}Pb/^{207}Pb$ up to 1.173). The increase of lead pollution detected in the Belgian peat is synchronous with intense mining and metallurgical activity that took place all over NW Europe and around the Mediterranean Sea. In addition, a local

327  pollution may have occurred in MIS and CLE sites. The Pb isotopic values of CLE and MIS samples
328  ($^{206}$Pb/$^{207}$Pb ~ 1.170-1.180) from 20 BC to AD 400 show good agreement with the isotopic field of the
329  Belgian Pb–Zn ores ($^{206}$Pb/$^{207}$Pb ~ 1.167-1.180). In Belgium, there is no historical, archaeological
330  evidence for Roman Pb–Zn mining. However, in previous studies of a peat column taken nearby an
331  archaeological site constituted by a Roman road and peat bog core in the Hautes Fagnes, Renson et
332  al., [44] and De Vleeschouwer el al., [43] found and dated very high Pb concentration (up to 90-135 µg
333  g-1) that reflect a local pollution linked to the Roman road [44]. Additional, the Pb isotopic
334  composition found by De Vleeschouwer el al., [43] and Renson et al., [44] are in good agreement with
335  isotopic composition of Pb–Zn ores from the Verviers syncline located 15 km northwards to the
336  Hautes Fagnes Plateau. In MIS core where the maximum of Pb concentration > 60 µg g-1, it seems
337  that a local influence has been recorded. In CLE core, where the maximum of Pb concentration (> 15
338  µg g-1) is lower than in MIS core, it seems that the local influence is less recorded.

339     Many other studies have reported Pb contamination dating from the Roman period, including
340  peat bogs [e.g., 1, 13; 80], lake sediments [e.g., 80-83 and ice cores [84-85] (Fig.5). During this interval
341  period, production of Pb in Europe and Asia reached approximately 80,000 tons per year [18]. It has
342  been estimated that as much as 5% of this Pb production might have been emitted to the atmosphere
343  [86] and was registered in most natural archives from both low and high latitudes. Our results from
344  CLE and MIS cores are consistent with the timing of documented Roman lead deposition in other
345  lake, peat bog and ice archives (Fig. 5). Most of those studies shown a peak of lead concentration
346  somewhere between 50 BC and AD 200. As an exception the increase in atmospheric Pb concentration
347  was recorded around 200 BC in England [1; 87] and Spain [13]. These findings suggest the existence
348  of an earlier Pb extraction industry (pre-Roman mining activities) in the British Isles and Spain. Our
349  geochemical results yield evidence of local and regional environmental contamination in the Belgian
350  peats due to mining activities that began during Roman period.

351

352   Figure 5: Lead records from : A. Belgian peat cores for the period from 500 BC to AD 500 [this study,

353   44], B. NW Spain peat core [13], C. England peat cores [1,87], E. French lake sediments [83], F. Swedish

354   lake sediments [81-82], G. Suiss ice core [85], H. Canadian ice core [84]. The historical production of

355   lead during Roman period [14].Yellow zone corresponds to zenith Roman Empire.

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### 4. Conclusion

The Clefaye and Misten bogs in Eastern Belgium provides a high-resolution record of the Pb AR and Pb isotope signatures during the Roman period. The study of several cores reveals the heterogeneity in peat accumulation. The highest Pb concentration and $EF_{Pb}$ were observed between 50 BC and AD 215 (15-60 µg g$^{-1}$, 105-115; respectively). Pre-Roman Pb AR averaged 0.1-0.4 mg m$^{-2}$ yr$^{-1}$ from 500 BC to 100 BC, Roman Pb AR reach a maximum from 0.7 to 1.2 mg m$^{-2}$ yr$^{-1}$ between 50 BC and AD 215. Pb contamination decreased significantly before the end of the Roman period. The amplitude of Pb AR and chronologies in the CLE and MIS cores are consistent with those reported for other European peat records, reflecting the influence of regional European pollution. High Pb AR values during the Roman period were primarily caused by mining and metallurgical activities. This study completes the European datasets for pollution reconstruction during the Roman period.

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