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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 of uranium and thorium. The isotopic composition of lead ores is usually different from that of bedrock [8]. Consequently, lead isotopes enable to discriminate between Pb sources of pollutants and

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Pb derived from the erosion of the Earth crust. Lead isotopes ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb) have been often used as evidence of anthropogenic heavy metal pollution, particularly in peatlands [e.g., 2, 5, 9-13].

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

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

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

In this work, high-resolution records of Pb concentrations and stable Pb isotopic compositions in two ombrothrophic peat collected from Haute Fagnes Plateau (SE Belgium) are used: 1) to track the

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history of Pb pollution in Belgium during the Roman period; 2) to identify the Pb supplies and; 3) to reconstruct the historical evolution of Pb pollution in comparison with other European archives.

2. Materials and methods

2.1. **Sampling and preparation**

The present study is focused on the sections covering Roman period of two ombrotrophic peats located in a nationally protected peatland area, the Hautes-Fagnes Plateau in East Belgium (Fig. 1B-D). The Hautes-Fagnes Plateau is part of the Stavelot Massif, mainly composed of lower Paleozoic quartzites and pyllades [53]. The geological substratum is covered by post-Paleozoic sediments (clays of alteration, continental and marine sands, loess – [54]) with some occasional outcrops of Early Cambrian (Revinian) quartzites. Core MIS-08-01b (750 cm) was taken in February 2008 from the Misten bog that is made of an accumulation of 8 m (estimated by a radar surface prospecting –[55]) of Holocene peat [43]. Core (CLE-15-01b, 550 cm) was taken in July 2015, from Clefaye bog, which the maximum peat thickness reaches up to 5.5 m [55] and the complete peat deposit section spans about 7000 years. The two ombrotrophic peats studied lie just 8 km apart.

The top 100 cm of the two cores was sampled by using a titanium Wardenaar corer [56]. The lower peat core was cored with a Belorussian corer [57]. Since we mainly focus our study on the Roman period, 60 cm from Clefaye bog (from 165 to 225 cm) and 90 cm from Misten bog (from 90 to 180) which represents ~1000 yrs history (from 500 BC to AD 500) were used. Core sub-samples of 1 cm thick slices were taken according to the protocol defined by Givelet et al. [58]. In Clefaye bog, the sample slices were sub-sampled into three. A part of the sample slice was freeze-dried, then mechanically-ground, using an agate ball mill at the University of Liège, to measure the degree of humification, stables isotopes. The second part was used for geochemical analysis and the remaining core samples were stored for further analyses, including dating. The Misten core was previously studied by Allan et al., [2, 59-60] and Fagel et al. [61] for its chronology, atmospheric dust flux and paleoenvironmental changes.

2.2. Elemental geochemistry and Pb isotope analyses

The samples from each core were analyzed separately using different methods as they were initially part of two different studies.

2.2.1. CLE-15-01b core (CLE)

According to De Vleeschouwer et al. [62] and Boes and Fagel [63], CLE samples were subsampled at 4 cm-long and 0.5 cm-thick slices and impregnated in order to consolidate them before to analyze scandium (Sc), Titanium (Ti), Aluminum (Al) and Lead (Pb) concentrations. The concentrations were determined by Laser Ablation Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) connected to an ESI New Wave UP-193FX Fast Excimer ArF laser of 193 nm at the Royal Museum for

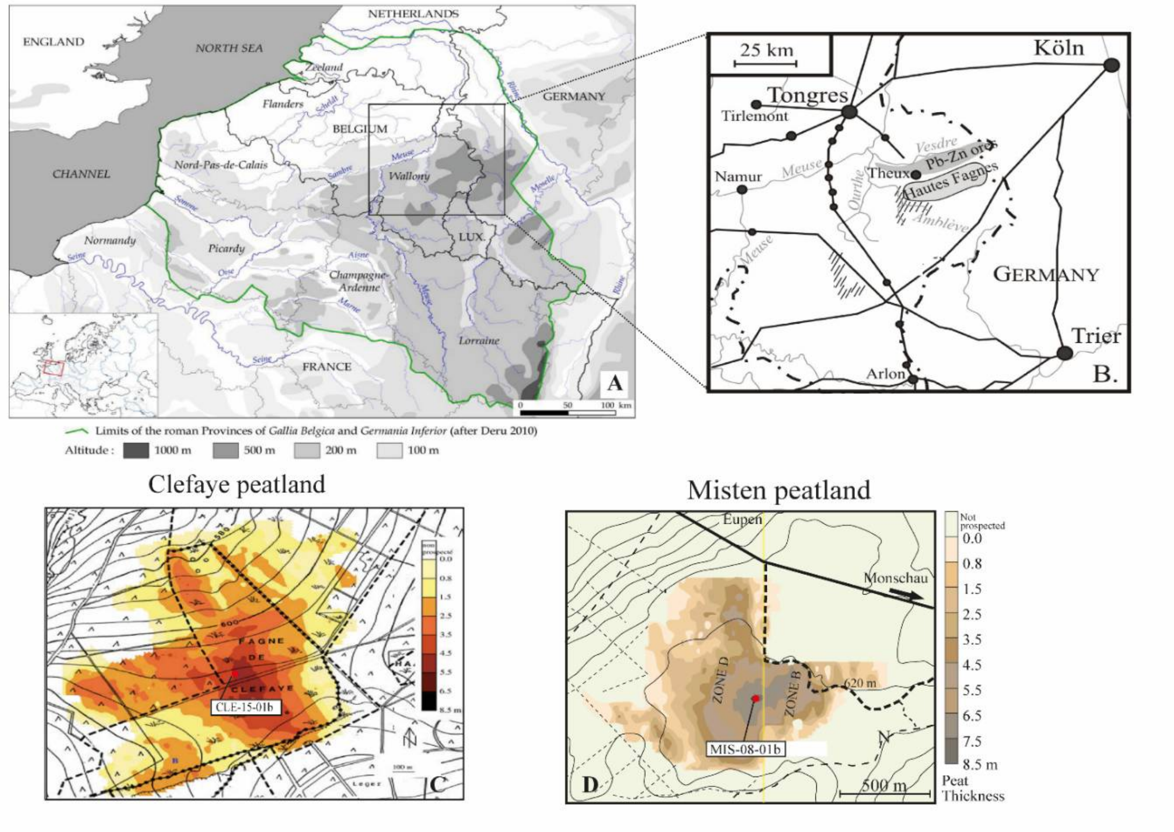

Figure 1: A. Localisation of Belgium as a part of Gallia Belgica (northern France, western Germany, southern Netherlands and Belgium)(after Deru [88]), B. Location map of the Hautes Fagnes Plateau and the Pb–Zn ores of E-Belgium (modified from De Vleeschouwer et al., [43]), C and D. Radar derived peat 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

NBS981 standard was repeatedly measured in alternation with samples in order to control any daily instrument drift. The isotope ratios of the NBS981 standard were stable during the analysis session [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 (2s)]. These values are consistent with the recommended values and are in agreement with the 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 ± 0.0006, n = 350).

Table 1: Pb isotope data of the CLE and MIS cores measured MC-ICP-MS. Starts correspond to 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 ($r_{\text{Al-Sc-Ti}} > 0.6$, 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).

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

Table 1 summarizes results of Pb isotope analyses in both cores CLE and MIS. In core CLE, the $^{206}Pb/^{207}Pb$ ratio shows two main ranges: from 400 BC to 170 AD, the ratio drops from 1.182to 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 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 it increases to 1.188±0.00001 at AD 500.

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

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

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

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

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 cores EF_{Pb} values remain low from 500 to 200 BC and increase to reach a maximum between AD 50 and AD 225 for CLE and between 60 BC and AD 200 for MIS. Finally, EF_{Pb} values decrease toward the upper section of cores. The location and assigned chronology of the maximum EF_{Pb} differ in each core. Nevertheless, the increase in EF_{Pb} values in each core is coincident with the period of Roman mining activities.

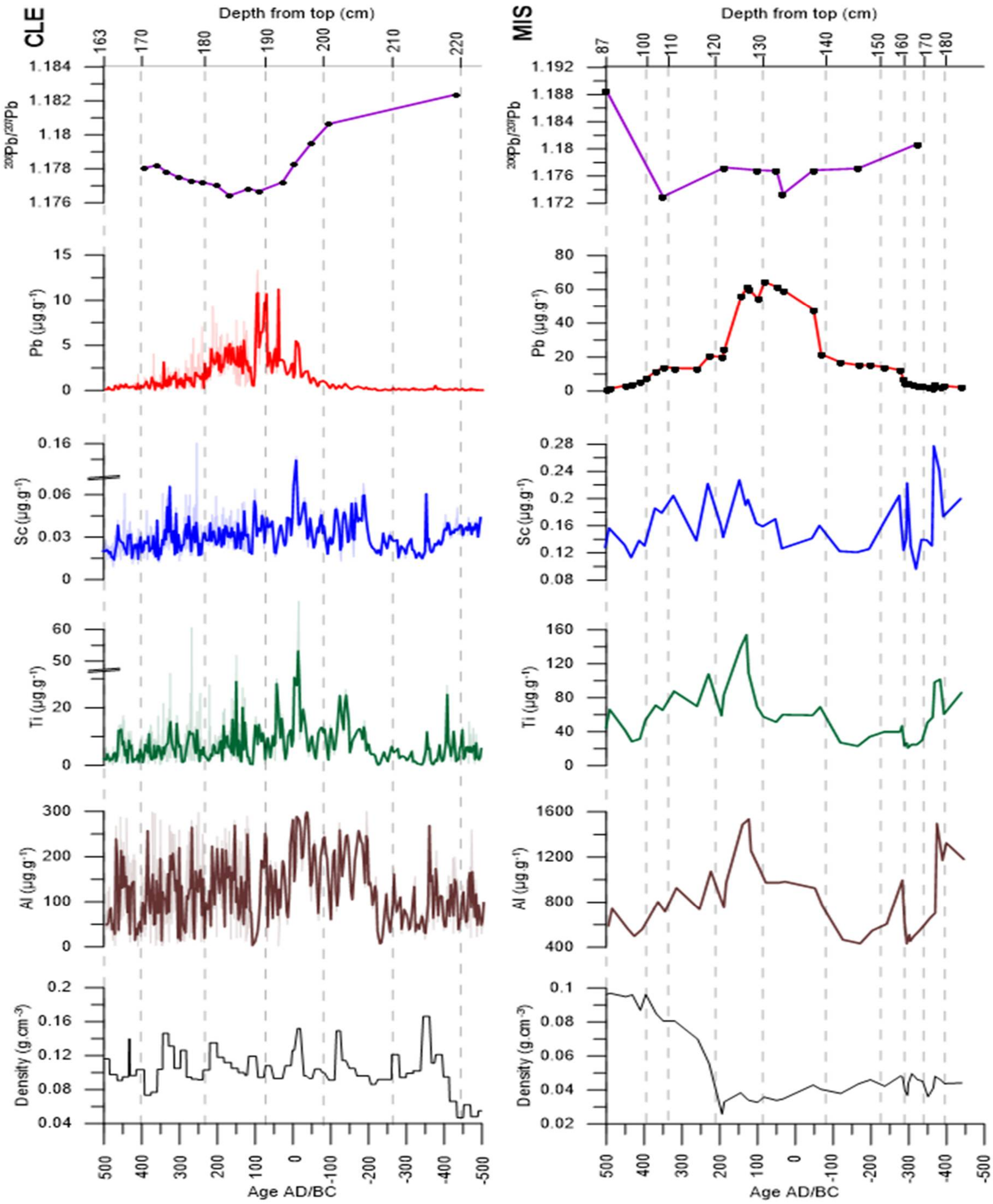

Figure 2: Evolution of density, elemental concentrations (Al, Ti, Sc and Pb), and radiogenic isotope ^{207}Pb/^{206}Pb ratios versus age and depth in CLE and MIS cores.

The use of trace element accumulation rates (AR) instead of concentrations or enrichment factors is more appropriate, as variations in net peat accumulation and decomposition are taken into account. The peat accumulation rate varies within a profile and differences between cores profiles can be caused by differences in surface growth rates and in decomposition rates because peat compaction increases with decomposition. Based on age-depth model, density and [Pb], the Pb accumulation rate can be calculated as follow:

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

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 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 80 BC (Fig.3), then it increases from the inception of the Roman period at 50 BC to reach a maximum 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 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 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 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 period (i.e., after AD 350). During the Roman period, the maxima Pb AR are characterized by values higher than 25-30 times the natural background values (< 0.03 mg m^{-2} yr^{-1} in CLE and < 0.07 mg m^{-2} yr^{-1} in MIS).

An intra-site variability in Pb AR values is observed when CLE and MIS cores are compared. During both the pre-Roman and Roman periods Pb AR at MIS is higher than at CLE. However, they both indicate similar chronologies of the Pb AR. As the two bogs are influenced by similar climate regime (nearby bogs located ca. 8 km of distance and similar altitudes), an actual difference in Pb AR values at the two sites is unlikely. Such difference may be explained by the within-bog spatial heterogeneity and/or the Pb measurement resolution. The difference between hummocks and hollows is well established, where hummocks are known to have higher interception of atmospheric particles [2]. Indeed, the MIS core was taken from a hummock and CLE was taken between a hummock and a hollow. Therefore, MIS may have better trapped atmospherically deposited Pb than the CLE bog due to a favorable micro-topography. The Pb concentrations were measured in the core CLE by LA-ICP-MS with a resolution of 1 mm and by ICP-MS in the core MIS with a lower resolution of 2 cm. This suggests that particle deposition has been affected by the micro-topography in this study.

The mean natural background of Pb AR (before 500 BC, 0.005 ± 0.002 mg m^{-2} y^{-1}-; unpublished 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 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]. Such comparison suggests that Pb AR values in CLE and MIS cores before 500 BC correspond to deposition of geogenic Pb. The dramatic increase in Pb AR recorded in CLE and MIS cores (from 50 BC to AD 200) is in good agreement with other studies on European peats which show a peak due to Roman Pb mining [1, 5, 13]. The maxima Pb AR in the CLE and MIS peat cores are within the range 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 in good agreement with the maximum values recorded in Spanish peat bogs (0.3-0.9 mg m^{-2} y^{-1}) which 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]. In a Swiss peat bog core, the maximum Pb AR is 37 times the background value for the Roman period [5]. Le Roux et al., [1] also showed that the maximum Pb AR value (0.22 mg m^{-2} y^{-1}) during the Roman period was 34 times higher than that of the pre-Roman period. In peat bogs cores from southern Black forest-SW Germany, Le Roux et al. [38] showed that the Pb AR is more than 40 times the background 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 MIS cores are consistent with those reported for other European peat records. The increase Pb AR obtained from the two cores is a valid indication of an increase of the atmospheric pollution during the Roman period.

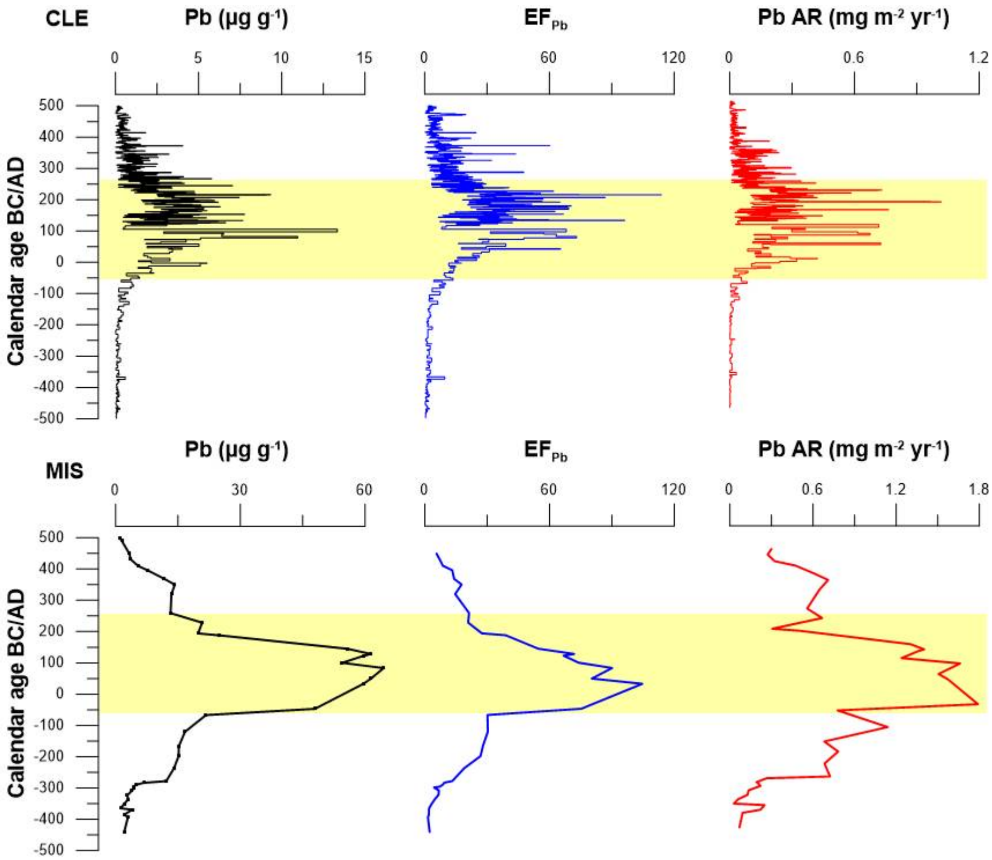

Figure 3: Summary of Pb concentration, EF$_{Pb}$, and calculated Pb AR (in mg m^{-2} yr^{-1}) for CLE and MIS cores. Yellow zone corresponds to zenith Roman Empire.

3.3. Identification of Pb sources

Roman mining and metallurgical activities all over NW-SW Europe and around the Mediterranean Sea increased significantly the amount of atmospheric Pb [e.g., 5, 15, 20, 61, 74 61]. The Pb isotope ratios deposited in CLE and MIS peat cores vary from 1.729 to 1.178 for ^{206}Pb/^{207}Pb ratios and from 2.086 to 2.089 for ^{208}Pb/^{206}Pb ratios (Fig.4).

In order to identify the source of lead, our Pb isotope data are compared with Belgian ores and Pb–Zn ores from the Verviers syncline exploited during the Roman period [75-76], Germany ores [77], Benelux modern aerosols [78], the Belgian pre-industrial background [43- This study] and the Upper Continental Crust [79]. In the binary diagram ^{208}Pb/^{206}Pb vs. ^{206}Pb/^{207}Pb, most of the CLE and MIS core data plot in the isotope field defined by Belgian ores [75-76], Eifel ores [77], Pb–Zn ores from the Verviers syncline [75-76] (Fig.4). The Pb isotope ratios measured in CLE and MIS samples for the Roman period between 40 BC and AD 300 correspond to the isotopic fields of the Pb-Zn ores of the Verviers syncline, Belgian ores and the Eifel ores [77]. Most samples from the post/pre-Roman period have mixed Pb isotopic signatures between those of Belgian ores and that of the Belgian pre-industrial background. Note our results are consistent with those obtained by De Vleeschouwer et al. [43] in a former core recovered in the Misten bog and by Renson et al. [44] from peat columns (RC1) in the Hautes Fagnes Plateau (Fig. 4). The Pb isotopic ratios of this study show that the Clefaye and Misten peats are influenced by a mixture of local and regional anthropogenic sources.

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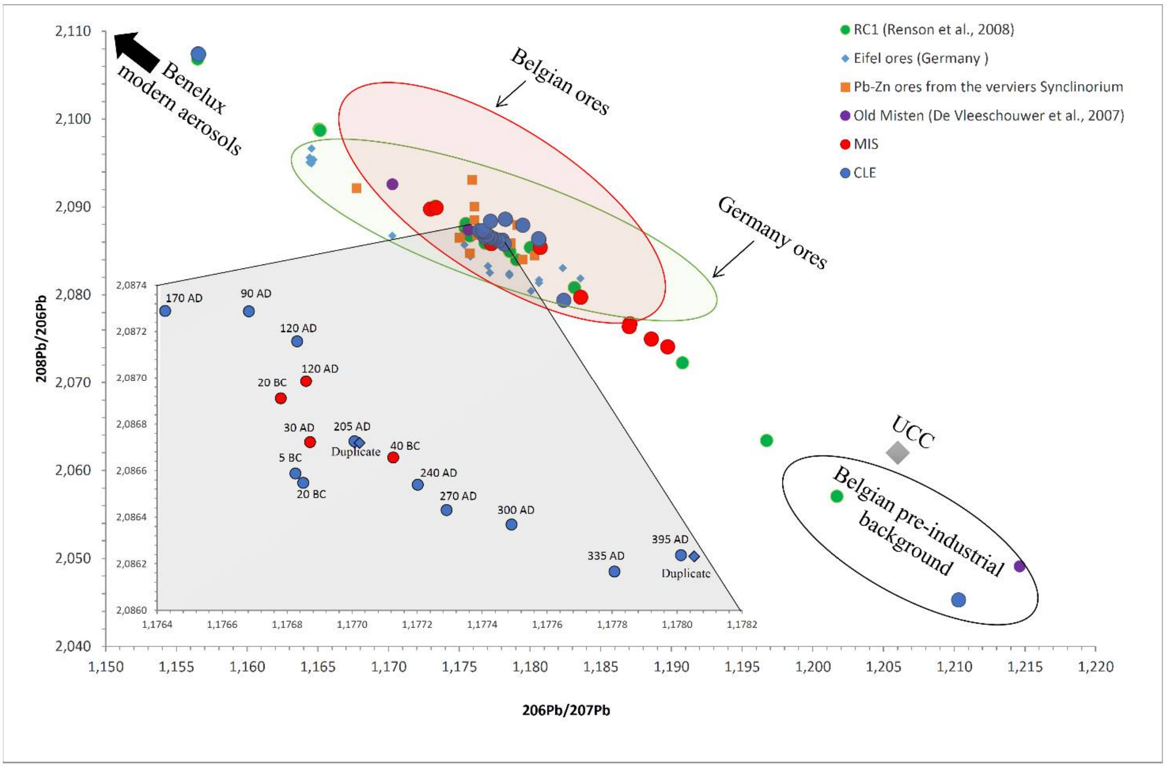

Figure 4: Binary diagram ^{206}Pb/^{207}Pb vs ^{208}Pb/^{206}Pb. Benelux modern from Bollhöfer and Rosman [78]. Belgian ores and Pb-Zn ores from the Verviers Synclinorium from Cauet and Herbosh [75] and Dejonghe [76]. German ores from Durali-Mueller et al., [77]. Belgian pre-industrial background from 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$_{\mathrm{Pb}}$ 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 pollution may have occurred in MIS and CLE sites. The Pb isotopic values of CLE and MIS samples ($^{206}Pb/^{207}Pb$ ~ 1.170-1.180) from 20 BC to AD 400 show good agreement with the isotopic field of the Belgian Pb–Zn ores ($^{206}Pb/^{207}Pb$ ~ 1.167-1.180). In Belgium, there is no historical, archaeological evidence for Roman Pb–Zn mining. However, in previous studies of a peat column taken nearby an archaeological site constituted by a Roman road and peat bog core in the Hautes Fagnes, Renson et al., [44] and De Vleeschouwer el al., [43] found and dated very high Pb concentration (up to 90-135 µg g-1) that reflect a local pollution linked to the Roman road [44]. Additional, the Pb isotopic composition found by De Vleeschouwer el al., [43] and Renson et al., [44] are in good agreement with isotopic composition of Pb–Zn ores from the Verviers syncline located 15 km northwards to the Hautes Fagnes Plateau. In MIS core where the maximum of Pb concentration > 60 µg g-1, it seems that a local influence has been recorded. In CLE core, where the maximum of Pb concentration (> 15 µg g-1) is lower than in MIS core, it seems that the local influence is less recorded.

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

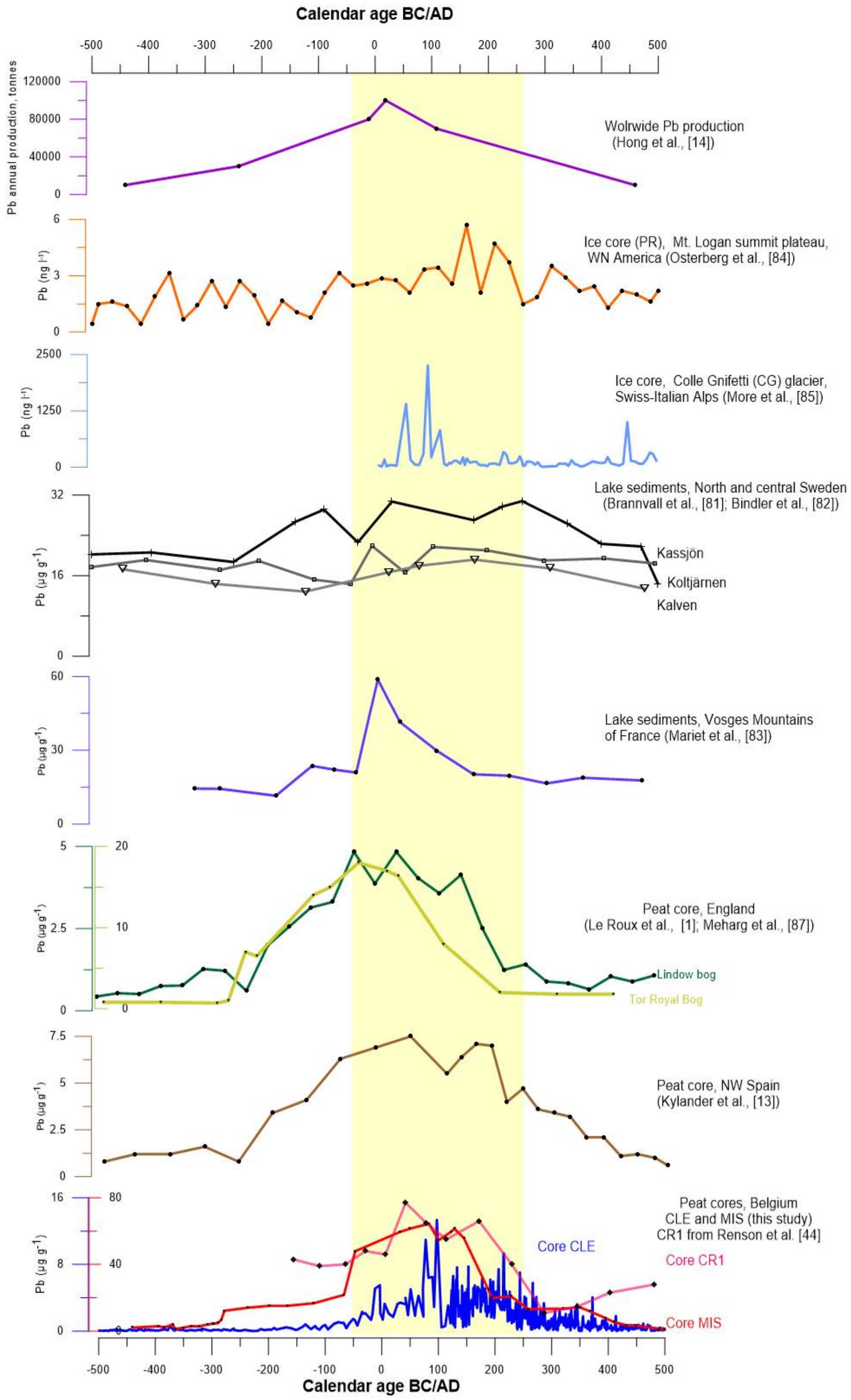

Figure 5: Lead records from : A. Belgian peat cores for the period from 500 BC to AD 500 [this study, 44], B. NW Spain peat core [13], C. England peat cores [1,87], E. French lake sediments [83], F. Swedish lake sediments [81-82], G. Suiss ice core [85], H. Canadian ice core [84]. The historical production of lead during Roman period [14].Yellow zone corresponds to zenith Roman Empire.

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.

Author Contributions: M. Allan, and N. Fagel designed the experiments, N. Mattielli carried out Pb isotopes data analysis. M. Allan prepared the manuscript with contributions from all co-authors.

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