

# Atmospheric lead and heavy metal pollution records from a Belgian peat bog spanning the last two millenia: Human impact on a regional to global scale

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## Abstract

Europe has been continuously polluted throughout the last two millennia. During the Roman Empire, these pollutions were mainly from ore extraction and smelting across Europe. Then, during the Middle Ages and the Early times of Industrial revolution (i.e. 1750), these pollutions extended to coal burning and combustion engine. Belgian ombrotrophic peat bogs have proved an effective archive of these pollutants and provide the opportunity to reconstruct the history of atmospheric deposition in NW Europe.

The results of recent and past trace metal accumulation and Pb isotopes from a one-meter peat core (in the *Misten* peat bog) have been derived using XRF and Nu-plasma MC-ICP-MS. Combined with <sup>14</sup>C and <sup>210</sup>Pb dates these data have enabled us to trace fluxes in anthropogenic pollution back to original Roman times.

Several periods of well-known Pb pollution events are clearly recorded including the Early and Late Roman Empire, the Middle Ages and the second industrial revolution. Also recorded is the introduction of leaded gasoline, and more recently the introduction of unleaded gasoline. Lead isotopes in this site have also enabled us to fingerprint several regional and global sources of anthropogenic particles.

**Keywords:** Peat; Geochemistry; Belgium; Pollution; Last two millennia

## 1. Introduction

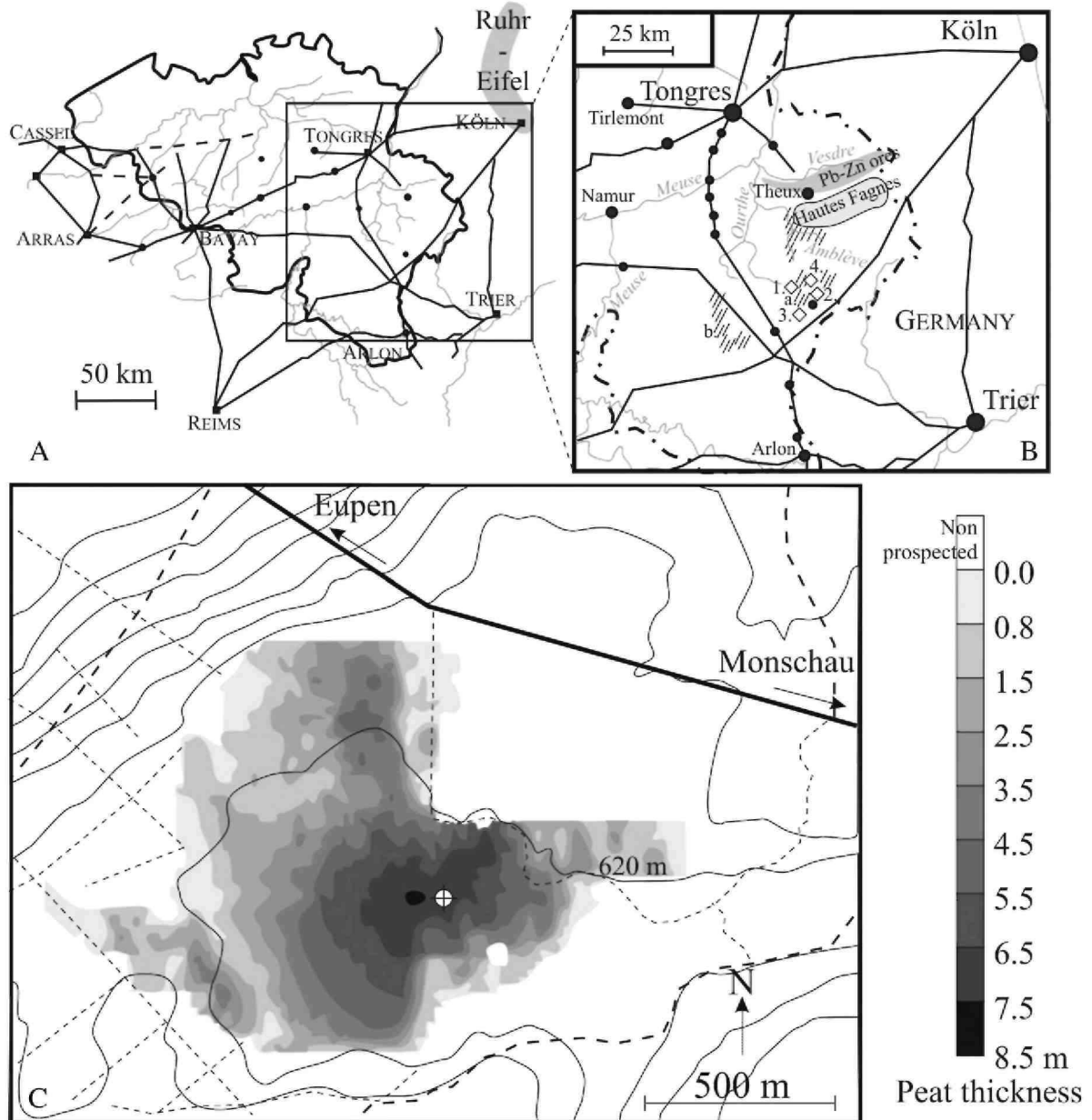
Centuries of atmospheric pollution caused by industrial activities, coal burning, and petroleum use has left an indelible mark in Europe's soils in the form of heavy metals. The fallout of these anthropogenic aerosols mix with natural aerosols, for example from rock weathering become incorporated into the soils where they are preserved. Over time the release of these heavy metals including lead, zinc, copper, and nickel, which well exceed natural levels (Boyd, 2004), can contaminate the soil and surrounding land.

Peat bogs are particularly sensitive archives of human activities and more specifically of atmospheric pollution (e.g. Shotyk et al., 1996, 2003; Weiss et al., 2002; Martinez-Cortizas et al., 2002; West et al., 1997; Mighall et al., 2002; Novak et al., 2003; Le Roux et al., 2004). Most importantly, peat is particularly effective at preserving atmospheric metal deposition in the form of lead (e.g. Shotyk, 2002; Shotyk et al., 1998, 2003; Vile et al., 1999; Weiss et al., 1999), copper (Rausch et al., 2005; Mighall et al., 2002), nickel (Krachler et al., 2003) and zinc (Rausch et al., 2005; Twardowska et al., 1999). Recent research has shown that ancient Pb contamination in peat can be traced by Pb isotopes and fingerprinted to a local or regional origin (e.g. Kempter and Frenzel, 1999; Monna et al., 2000; Le Roux et al., 2004; Kylander et al., 2005). The more recent atmospheric Pb pollution (i.e. coal burning and leaded gasoline) is shown to be more regional or even continental (Dunlap et al., 1999; Véron et al., 1999; Le Roux et al., 2005; Shotyk et al., 2005).

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**Fig. 1:** A. General map showing the Roman road system (redrawn after Corbiau, 1998). The actual Ruhr-Eifel Region is also reported. Plain lines: Roman road system. Black circles: principal Roman cities and village (size of the circles gives an idea of the relative importance of each city). Grey lines: river system. B. Location map of the Hautes Fagnes Plateau and its surroundings. Dashed area: alluvial mounds remaining from gold prospecting, <sup>14</sup>C-dated at A: 120 B.C.-140 A.D. and B: 400 B.C.-200 B.C. Diamonds: 1. the gold mine gallery with dated wooden piece; 2. the open-air gold mine (undated); 3. sites with roman graves; 4. site with Roman coins. Plain lines: Roman road system. Black circles: principal roman cities and village (size of the circles gives an idea of the relative importance of each city). Grey lines: river system. Pb-Zn ores: lead-zinc ore deposit (after Dejonghe, 1998). C. Radar derived peat thickness of the Misten bog (modified after Wastiaux and Schumacker, 2003). Altitude lines are 5 m distant in altitude. The different dotted lines are forestry ways. Coring location is reported by the open circle.



The Hautes Fagnes Plateau (SE Belgium), the largest peatland area in Belgium, is located in an intermediate position in Western Europe (surrounded by France, U.K. and Germany). The Hautes Fagnes Plateau is also situated to the South of Pb-Zn ore deposits (extracted between the 19th and 20th centuries; Dejonghe, 1998) and nearby the German border which is 300 km from the Region of the Ruhr-Eifel industrial area. In more ancient times the Hautes Fagnes plateau was surrounded by several Roman sites. On the site several archaeological (Cauet, 2005; Renson et al., 2005, 2007; Remy 1981) and historical (Graillet, 1998) investigations support Roman occupation and ore mining in the area (see Sections 4.1 and 4.2).

In this paper, we present the elemental records of Si, Ti, Sr, Pb, Cu, Zn and Ni for the top meter of a peat core from the Misten Bog from the Hautes Fagnes Plateau. Si and Ti were used as evidence for periods of enhanced atmospheric particle and Sr is used to demonstrate the ombrotrophic character of the bog. Ti is also used as a reference element for the calculation of enrichment factors. A Pb isotopic study is also presented in order to decipher from the possible lead pollution sources. The main aim of this study was to use the results of a high resolution investigation of heavy metal pollution in a peat core from Misten Bog to reconstruct the pollution history of the Hautes Fagnes and in turn, contribute to the pollution history of Europe.

## 2. Material and methods

### 2.1. Site description

The Misten bog is located in the Northern part of the Hautes Fagnes Plateau, 5 km from the German border (Fig. 1A). It is a law-protected raised bog accumulating more than 8 m of peat (Wastiaux and Schumacker, 2003), dating back to 9000 years ago (Persh, 1950; Gérard, 2004). The first meter of the Misten bog is composed of young *Sphagnum imbricatum* peat with *Eriophorum* fragments. Between 30 and 20 cm, sphagnum species also include aquatic species like *Sphagnum cuspidata* (Persh, 1950).

### 2.2. Sampling and sample preparation

In summer 2003, a 1 m long, 10 cm diameter core was retrieved using a Belorussian-type stainless steel D-corer (Belokopytov and Beresnevich, 1955; Jowsey 1965). The inner parts of the corer are coated with Teflon® adhesive to avoid metal contamination by the coring device. Cores were bagged into PVC tubes and wrapped in plastic. The 1 m core was cut into 1 cm slices in the laboratory using clean plastic tools. Each sample was dried (105 °C, 12 h) and then ground twice: (1) manually using an agate mortar; (2) mechanically in agate jars pulverisette (400 rpm for 1 h). The mortar and jars were cleaned between each samples using tap and then mQ water, and finally air-dried.

### 2.3. XRF analyses

An average of 3.5 g of peat powder was pressed into pellets at 200 kN/cm<sup>2</sup>. Pellets were analyzed using ARL 9400 XP XRF spectrometer (University of Liège) for the following elements: Si, Ti, Sr, Ni, Zn, Cu and Pb. Calibrations were made using international standards: coals (CLB-1, NIST 1632b et NIST 1635), lichen (BCR-482), pond sediments (NIES-2), tea leaves (NIES-7), vehicle exhaust particulates (NIES-8) and sediments (JSD-2, JSD3, SGR). Reproducibility, accuracy and detection limits are summarized in Table 1. Sediments and vehicle exhaust particle standards were used in order to extend the concentration range to higher values often occurring in highly polluted recent peat layers. Measured sample concentrations are presented in Table 2.

**Table 1:** Mean statistics calculated on the analyzed standards (see text)

	Si	Ti	Sr	Cu	Pb	Ni	Zn
Mean DL	0.18	70	3.7	1.5	3.2	1.3	1.4
Mean QL	0.55	210	11.1	4.6	9.7	3.8	4.2
Mean error	0.5	4.7	4.6	5.2	6.5	20.5	14.7
Mean reproducibility	97	96	98	75	87	93	96

Mean DL: mean detection limit (i.e.  $3\sigma$ ); Mean QL: mean quantification limit (i.e.  $9\sigma$ ). Both are in % for Si and in ppm for other elements, respectively. Mean error (%;  $n=10$ ) =  $100 \times [\text{mean standard values} - \text{certified or suggested values}] / \text{certified or suggested values}$ . Mean reproducibility (%;  $n=10$ ) =  $100 \times [\text{mean standard values} - \text{standard deviation}] / \text{mean standard values}$ .

### 2.4. Measurement of heavy metals in deep peat samples

Two samples from the bottom of the bog (660 and 678 cm depth, Table 2) were analyzed to establish natural background concentrations. As their elemental content could be expected to be very low and thus under XRF detection limits, these two samples were acid digested in clean air cabinets (University of Liège). Acid digestions consisted of a two-step dissolution in closed Savilex® beakers: (1) addition of H<sub>2</sub>O<sub>2</sub> 30% p.a. and HNO<sub>3</sub> 65% cc. sub. in a proportion of 3:1 for organic matrix dissolution, and (2) addition of HF suprapur (Merck)+HNO<sub>3</sub> 65% cc. sub. of 1:6 for mineral matrix dissolution. The beakers were placed on a hot plate at 130°C for 4 days. After drying, 0.5N HNO cc. sub. was added to obtain the solution. Analyses were performed on ICP-AES (IRIS Advantage) at the MRAC-Tervuren (Belgium). Calibrations were made with In-Ru-Re-Bi internal standards (10 and 20 ppb) and two international reference materials: CRM-100 beech leaves (EU

certificated) and granite GA (Govindaraju and de la Roche, 1977). Accuracy was between 1-11% for major elements and 1-2% for trace metals. Detection limits were lower than 1 ppm for major elements. Detection limits for trace metals and other trace elements were lower than 1 and 10 ppb, respectively.

## 2.5. Acid digestion for lead isotope analyses

All the samples were processed in clean air cabinets (University of Liège and University of Brussels, Belgium). 50 mg of original dry powder was acid-digested as previously described at Section 2.4, to which was added a further step. After drying, 6 N HCl was added and the perfectly pure solution obtained was slowly evaporated. The dried residues were dissolved in HBr 6% cc. sub. prior to the chromatographic separation.

Lead chemistry was performed by a single passage through anionic exchange micro-columns following the protocol of Weis et al. (2005). Distilled (HNO<sub>3</sub>) or sub-boiled (HCl, HBr) acids were used during the chemical treatment. Total procedural Pb blanks ranged from 0.1 ng to 0.4 ng and were negligible regarding Pb contents in 50 mg of sample (615 ng at 28.5 cm<Misten content<4745 ng at 3.5 cm).

Lead isotopic ratios were measured on a Nu Instruments Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at University of Brussels during four analysis sessions of 5 days in total.

Configuration of the collector array enabled simultaneous collection of Pb (for masses 208, 207, 206, 204) together with Tl (205, 203) and Hg (202). Hg was used to correct interferences on mass 204 (because of <sup>204</sup>Hg). Tl is added to all samples and standards to monitor and correct instrumental mass fractionation. All standard and sample solutions were prepared to obtain a Pb/Tl ratio of ~ 5, a signal of ~ 100 mV on the axial collector (<sup>204</sup>Pb), and to match the Pb, Tl concentrations of the standards (200 ppb and 50 ppb, respectively). The NBS981 provided regular checks of reproducibility and drift during each day. Sixty-four analyses of the NBS981 Pb standard were completed gave mean values of <sup>208</sup>Pb/<sup>204</sup>Pb = 36.7164 ± 0.094 (2SD), <sup>207</sup>Pb/<sup>204</sup>Pb = 15.4969 ± 0.0036, <sup>206</sup>Pb/<sup>204</sup>Pb = 16.9401±0.0036, which are in agreement with the long-term internal laboratory reproducibility ( $n = \pm 1000$ , <sup>208</sup>Pb/<sup>204</sup>Pb = 36.7130 ± 0.012 (2SD), <sup>207</sup>Pb/<sup>204</sup>Pb = 15.4950 ± 0.004, <sup>206</sup>Pb/<sup>204</sup>Pb = 16.9393 ± 0.0044), the TIMS triple spike values (Galer and Abouchami, 1998) and other Nu Plasma published values (Weis et al., 2005). Replicates (i.e., a re-run of the same sample solution) are presented in Table 3.

## 2.6. <sup>14</sup>C and <sup>210</sup>Pb dating

A C measurement was performed on a bulk peat sample at 53.5 cm depth using Accelerator Mass Spectrometry (1.5 SDH-Pelletron Model "Compact Carbon AMS") at Poznan Radiocarbon Laboratory (Poland). This provided an age interval of 250 yr A.D.-401 yr A.D. (calibrated by Calib 5.0.2, Stuiver et al., 2005; Reimer et al., 2004) and a mean date of 326±76 yr A.D. [uncalibrated age of 1715±30 yr B.P, Poz-7012], Radionuclides (<sup>210</sup>Pb, <sup>214</sup>Pb) were measured using low background Gamma Spectrometry (GCW4028, HPGe, Canberra) in Heidelberg. The maximum depth at which unsupported <sup>210</sup>Pb could be detected is 10 cm. The age-depth relationship was calculated using the CRS model (Appleby, 2001). Errors on Pb age dating and peat accumulation rate were calculated by propagation of errors following the method of Appleby (op. cit.). These errors were rough estimations since the peat accumulation rate in the recent samples was very low. Results of these analyses are summarized in Table 4.

## 2.7. Calculation of enrichment factor

Lead Enrichment factor (Pb E.F.) was calculated in order to decipher anthropogenic lead inputs from lead of natural (i.e. crustal) origin. In line with previous similar geochemical investigations in peat (e.g. Shotyk et al., 2000; Kempter, 1996), Ti was used as a reference element, because its mineral phases (e.g. titanite, ilmenite or titanomagnetite) are resistant to alteration (Wedepohl et al., 1978; Nesbitt and Markovics, 1997). Lead enrichment factor was obtained as follows: Pb E. F. = ([Pb]sample/[Ti]sample)/([Pb]<sub>Upper crust</sub>/[Ti]<sub>Upper crust</sub>). Upper crust reference values (17 and 4100 ppm for Pb and Ti, respectively) were taken from Mc Lennan (2001).

**Table 2:** Elemental content along the top meter of a peat core from the Misten Bog

Depth	Si	Ti	Sr	Cu	Ni	Pb	Zn	Pb E.F.
0.5	4.32	1187	14.1	8.40	14.2	537	106	109
1.5	4.34	1206	17.2	12.3	18.3	647	133	130
2.5	3.41	1223	16.4	13.2	14.5	766	153	151
3.5	3.40	1048	19.1	18.7	22.8	949	214	218
4.5	3.67	1056	16.1	10.6	9.4	617	133	141
5.5	4.93	1066	16.7	8.71	7.2	413	117	93
6.5	3.60	785	14.5	5.60	3.9	299	106	92
7.5	2.60	677	15.7	4.63	4.9	265	135	95
8.5	1.98	585	13.6	2.70	<D.L.	207	120	85
9.5	1.97	576	12.7	2.08	<D.L.	139	105	58
10.5	1.48	549	10.4	1.80	<D.L.	89.1	91.6	39
12.5	1.53	592	12.6	1.80	<D.L.	61.6	105	25
14.5	0.58	272	10.5	1.70	<D.L.	32.3	97.3	29
16.5	0.53	232	13.5	2.40	<D.L.	40.6	135	42
18.5	0.61	259	10.2	2.70	<D.L.	31.9	91.8	30
20.5	0.44	174	12.9	2.50	<D.L.	32.1	107	45
22.5	0.31	153	17.0	2.20	<D.L.	28.7	123	45
24.5	0.46	200	15.3	2.20	<D.L.	25.0	102	30
26.5	0.42	191	12.9	2.00	<D.L.	19.0	70.5	24
28.5	0.66	302	10.3	<D.L.	<D.L.	12.3	47.1	10
30.5	0.63	272	13.6	1.60	<D.L.	13.5	52.1	12
32.5	0.47	236	13.4	2.50	<D.L.	22.4	50.6	23
34.5	0.38	197	13.2	2.10	<D.L.	20.7	42.8	25
36.5	0.59	259	12.4	2.40	<D.L.	21.3	34.2	20
38.5	0.33	138	12.9	2.90	<D.L.	24.9	33.8	44
40.5	0.28	154	14.9	3.00	3.70	28.9	28.8	45
42.5	0.33	165	15.6	2.50	<D.L.	22.2	23.0	32
44.5	0.37	159	16.8	2.00	<D.L.	19.4	18.3	29
46.5	0.39	145	18.0	3.90	4.00	35.0	17.7	58
48.5	0.37	146	16.0	3.30	3.50	30.9	14.5	51
49.5	0.41	159	18.1	4.47	6.69	39.5	16.7	60
50.5	0.61	223	17.0	5.70	13.1	84.6	34.2	92
51.5	0.41	154	16.4	6.08	10.9	58.6	16.7	92
52.5	0.30	116	14.1	4.70	7.30	45.2	12.5	94
54.5	0.32	136	13.4	4.10	6.40	43.2	9.20	76
56.5	0.48	138	13.8	4.10	6.50	43.8	8.80	76
58.5	0.63	195	12.9	4.40	7.80	47.4	8.60	59
60.5	1.25	318	9.30	<D.L.	<D.L.	32.3	<D.L.	25
64.5	0.67	233	7.50	<D.L.	6.43	57.9	<D.L.	60
68.5	0.79	228	6.99	<D.L.	3.85	60.4	<D.L.	64
72.5	1.54	468	7.91	<D.L.	4.28	82.9	<D.L.	43
76.5	0.52	193	7.80	<D.L.	4.25	81.8	<D.L.	120
80.5	0.70	252	10.6	<D.L.	<D.L.	139	<D.L.	133
86.5	0.65	254	6.97	<D.L.	<D.L.	95.1	<D.L.	90
88.5	1.07	335	6.96	<D.L.	6.19	98.7	<D.L.	71
96.5	0.36	98	8.53	3.06	7.26	60.9	<D.L.	150
98.5	0.44	144	9.11	10.2	12.4	69.1	<D.L.	116
660	-	2081	28.3	<D.L.	51.4	7.66	20.8	1
678	-	4215	63.9	11.38	50.4	16.1	18.1	1

<D.L.:under detection limits. Values in italic are semi-quantitative ( $3\sigma < x < 6\sigma$ ). bis-samples are replicates. Si concentrations are not measured for 660 and 678 cm samples because of SiF<sub>4</sub> volatilization during HF digestion.

**Table 3:**  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$  isotopic ratios

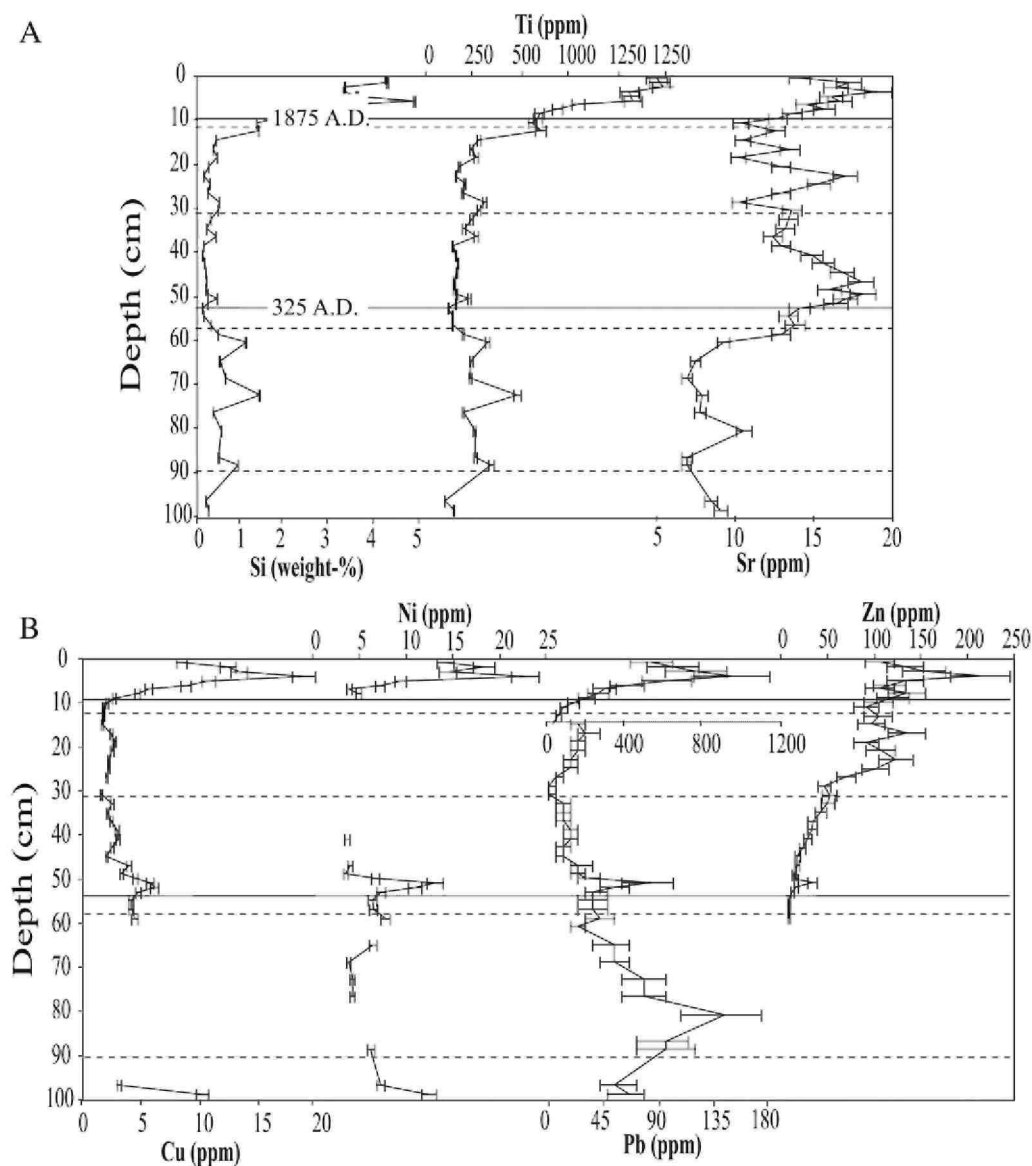
Depth	$^{208}\text{Pb}/^{204}\text{Pb}$	2se	$^{207}\text{Pb}/^{204}\text{Pb}$	2se	$^{206}\text{Pb}/^{204}\text{Pb}$	2se	$^{208}\text{Pb}/^{206}\text{Pb}$	2se	$^{207}\text{Pb}/^{206}\text{Pb}$	2se
0.5	37.9300	0.0030	15.5947	0.0011	17.9864	0.0012	2.1088	0.00180	0.8670	0.00010
0.5bis	37.9300	0.0040	15.5947	0.0015	17.9856	0.0017	2.1089	0.0023	0.8671	0.00020
2.5	37.9350	0.0020	15.5962	0.0008	17.9857	0.0009	2.1092	0.00110	0.8671	0.00010
5.5	37.8979	0.0031	15.5829	0.0013	17.9701	0.0017	2.1089	0.00009	0.8672	0.00002
5.5bis	37.9221	0.0034	15.5931	0.0014	17.9806	0.0016	2.1090	0.0001	0.8672	0.00003
8.5	37.9540	0.0020	15.5969	0.0007	18.0042	0.0009	2.1081	0.00110	0.8663	0.00020
10.5	37.9465	0.0041	15.5867	0.0015	18.0102	0.0017	2.1069	0.00008	0.8655	0.00002
15.5	38.1640	0.0030	15.6117	0.0011	18.2119	0.0014	2.0956	0.00160	0.8572	0.00030
20.5	38.1903	0.0032	15.6087	0.0013	18.2464	0.0014	2.0930	0.00009	0.8554	0.00003
24.5	38.1417	0.0038	15.6030	0.0013	18.1881	0.0016	2.0969	0.00007	0.8578	0.00001
30.5	37.9950	0.0060	15.5971	0.0023	18.0678	0.0025	2.1029	0.00350	0.8633	0.00020
40.5	38.1196	0.0027	15.6078	0.0011	18.1652	0.0015	2.0985	0.00011	0.8592	0.00004
50.5	37.9310	0.0060	15.5935	0.0024	17.9881	0.0029	2.1087	0.00310	0.8669	0.00050
50.5bis	37.9400	0.0040	15.5985	0.0014	17.9964	0.0016	2.1082	0.0024	0.8668	0.00020
52.5	37.9844	0.0043	15.5943	0.0015	18.0424	0.0017	2.1052	0.00010	0.8643	0.00003
52.5bis	37.9789	0.0079	15.5930	0.0030	18.0415	0.0022	2.1051	0.0001	0.8643	0.00003
56.5	38.1012	0.0094	15.5985	0.0038	18.1486	0.0049	2.1319	0.00007	0.8594	0.00003
88.5	38.3310	0.0040	15.6191	0.0015	18.3631	0.0020	2.0874	0.00200	0.8506	0.00050
98.5	38.2245	0.0041	15.6088	0.0015	18.2656	0.0018	2.0926	0.00008	0.8545	0.00003
660	39.0227	0.0065	15.6770	0.0056	19.0430	0.0029	2.0491	0.00006	0.8233	0.00002
678	38.9966	0.0033	15.6878	0.0009	19.2016	0.0013	2.0309	0.00004	0.8170	0.00001

se refers to standard error, i.e. derived from standard deviation.

**Table 4:** Pb age depth relationship in the 10.5 cm depth sample

Laboratory no.	Mean depth (cm)	Pb corrected date (year)	Uncertainty (year)
1	0.5	2003	0
2	1.5	1984	2
3	2.5	1964	5
4	3.5	1950	8
5	4.5	1938	10
6	5.5	1935	10
7	6.5	1920	16
8	7.5	1874	44
9	8.5	1835	28
10	9.5	1835	28
11	10.5	1813	57

**Fig. 2:** Concentration variations along depth for Misten bog (in % for Si and in ppm for other elements, respectively). C mean age for 53.5 cm sample (325 A.D.) and last Pb (10.5 cm; 1835 A.D.) sedimentation model derived-date are reported. Dotted lines represent the separation between five major intervals (see Sections 4 and 5 for further details). The x-scale of Pb profile is changed at 15 cm depth for visual commodity.



### 3. Results

#### 3.1. Elemental content

Elemental concentrations and lead E.F. of Misten bog are represented along depth in Fig. 2. For graphical presentation purposes, samples from levels 660 cm and 678 cm are not shown.

##### 3.1.1. Si, Ti

Both Si and Ti display a similar pattern of change with depth. Concentrations are low below 90 cm depth ( $[\text{Si}] < \sim 0.4\%$ ,  $[\text{Ti}] < \sim 120$  ppm), and increase to moderately between 90 and 55 cm depth ( $\sim 0.4\% < [\text{Si}] < \sim 1.5\%$ ,  $\sim 300 < [\text{Ti}] < \sim 1300$  ppm). These values are followed by a zone of minimum concentrations between 55 cm and 40 cm depth ( $\sim 0.28\% < [\text{Si}] < \sim 0.62\%$ ,  $\sim 150 \text{ ppm} < [\text{Ti}] < \sim 500$  ppm). Between 40 cm and 20 cm depth, a slight increase in concentrations can be detected ( $\sim 0.30\% < [\text{Si}] < \sim 0.70\%$ ,  $\sim 250 \text{ ppm} < [\text{Ti}] < \sim 850$  ppm). Finally, the concentrations increase significantly towards the surface of the bog ( $\sim 0.6\% < [\text{Si}] < \sim 5\%$ ,  $\sim 50 < [\text{Ti}] < \sim 500$  ppm).

### 3.1.2. Sr

Low Sr concentrations ( $[Sr] < 20$  ppm) were expected and are typical of peat from ombrotrophic bog (e.g. Shotyk, 2002). The two samples (660 and 678 cm depth) analyzed for natural background Sr gave a mean concentration of 46 ppm, a doubling concentration from the samples above the top meter. This higher concentration reflects the minerotrophic character of the peat, starting to accumulate just above the bottom sediment (loess and quartzite fragments).

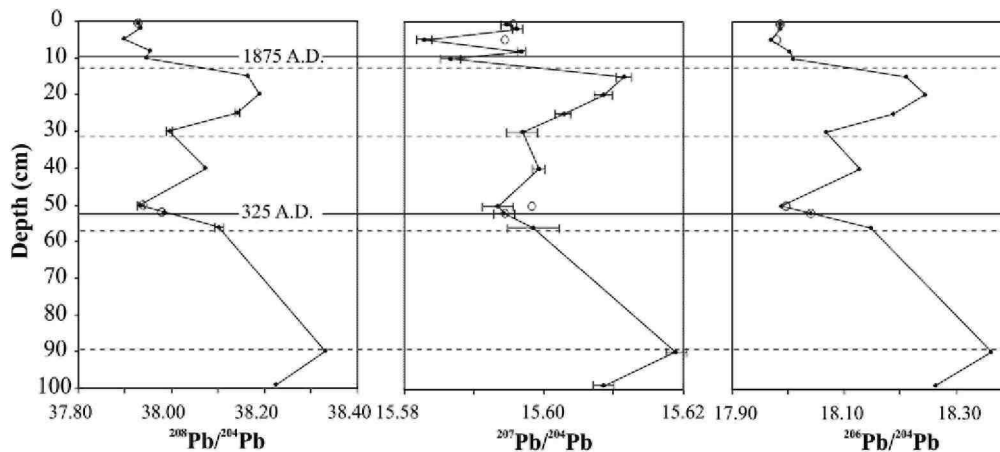
### 3.1.3. Cu, Ni, Pb, Zn

Between 100 cm and 50 cm, Cu and Zn concentration profiles are partially under detection limits (D.L.), and Ni concentrations are low. Pb concentrations do however show relatively high values (32.3 ppm to 139 ppm). For the top 50 cm of the core, values of Ni, Cu and Pb display similar trends, with minimum concentrations ( $[Pb] \sim 13$  ppm,  $[Zn] \sim 50$  ppm,  $[Cu] \sim 1.5$  ppm and  $[Ni] < D.L.$ ) at around 30 cm depth, with increased values ( $[Pb]$  up to 949 ppm,  $[Zn]$  up to 214 ppm,  $[Cu]$  up to 18.7 ppm and  $[Ni]$  up to 22.8 ppm) toward the surface.

## 3.2. Lead isotopic ratios

Profiles of lead isotopic ratios vs. depth are shown in Fig. 3.  $^{208}Pb/^{204}Pb$ ,  $^{207}Pb/^{204}Pb$ ,  $^{206}Pb/^{204}Pb$  isotopic ratios exhibit similar trends: poorly radiogenic values ( $^{208}Pb/^{204}Pb > 38.200$ ,  $^{207}Pb/^{204}Pb$  around 15.615,  $^{206}Pb/^{204}Pb > 18.250$ ) between 100 and 90 cm, and comparatively unradiogenic values ( $37.931 < ^{208}Pb/^{204}Pb < 38.120$ ,  $15.594 < ^{207}Pb/^{204}Pb < 15.608$ ,  $17.990 < ^{206}Pb/^{204}Pb < 18.165$ ) between 60 cm and 30 cm. Then ratios shift toward more radiogenic values between 30 cm and 10 cm ( $38.150 < ^{208}Pb/^{204}Pb < 38.200$ ,  $15.605 < ^{207}Pb/^{204}Pb < 15.615$ ,  $18.200 < ^{206}Pb/^{204}Pb < 18.300$ ) and in the top 10 cm show a sudden shift towards low isotopic values ( $^{208}Pb/^{204}Pb < 37.950$ ,  $^{207}Pb/^{204}Pb < 15.600$ ,  $^{206}Pb/^{204}Pb < 18.015$ ).

**Fig. 3:**  $^{208}Pb/^{204}Pb$ ,  $^{207}Pb/^{204}Pb$ ,  $^{206}Pb/^{204}Pb$  isotopic ratio vs. depth. Open circles are replicates.  $^{14}C$  mean age for 53.5 cm sample (325 A.D.) and last Pb (10.5 cm; 1835 A.D.) sedimentation model derived-date are reported. Dotted lines represent the separation between five major intervals (see Sections 4 and 5 for more details). Background samples (660 cm and 678 cm) are not represented.



## 4. Discussion

### 4.1. Si and Ti

#### 4.1.1. Historical and archaeological background in East Belgium

During the second Iron age (480 B.C. to 27 B.C.), Celts were established in South Belgium (Graillet, 1998; Remy, 1981). These people were the first important farmers and land clearers in the area, but their agricultural activities remained small compared to those of the following Roman period (Ferdrière, 1988). They were however known their mining activities. They developed gold extraction from, river overbank, river sediments, and arkose mines for making grinds (Cauuet, 2005; Remy, 1981; Graillet, 1998). Archeological evidence of



early gold mining in Southeast Belgium are attested by more than 1000 mining waste mounds (fluvial deposits) dumped near the source, mainly rivers and streams (Cauuet, 2005 and reference therein). Two of these mounds are found overlying peat. These provide respective radiocarbon age ranges of 120 B.C.-140 A.D. (Dumont, 1979; Gilot, 1997) and 400 B.C.-200 B.C. (Dumont, 1980; Gilot, 1997). Though it would be beneficial to confirm these data with further dates and field investigations, there are in good agreement with the Second Iron age and the Early Roman Empire.

Romans then extended land clearance for pasture and cultivation. Further evidence for pasture are shown in several pollen diagrams from peat sequences from the Hautes Fagnes. Indeed, *Plantago lanceolata* (considered as the best indication for pasture) made a first occurrence during the Neolithic, becoming more abundant during the Gallo-Roman period (Damblon, 1994). Cereal pollens indicative of increase anthropogenic activities were also found in significant amounts in the Hautes Fagnes representative of the Roman period (Damblon, 1994; Gotjé et al., 1990). Additional archaeological remnants from the Roman period are prolific in Belgium (Fig. 1B). Evidence of early mining activities include an open-air gold and arkose mine with grind remnants (Fig. 1B.2), and a mine gallery (Fig. 1B.3). (Cauuet, 2005; Remy, 1981). The open air mine is still not well dated and requires further archaeological investigation. Actually, the only link to the Roman period is made by field comparison with similar sites in France (Cauuet, 2005). In the mine gallery, a piece of wood used once used for propping up the mine shaft was dated to an age interval of 240 A.D.-440 A.D. (Cauuet, 2005) which corresponds to the Late Roman Empire period. However, as no evident archaeological artifacts of Roman facture have been found in this gallery, the age of gold extraction should be taken with caution. However, this piece of wood could represent later re-occupation of the mine. No further archaeological artifact of Roman age have been found to support this. Therefore the exact age of the extraction is still uncertain. There is no further evidence for metal mining or smelting Romans in the area. Moreover, from the 4th century A.D., a decline of the agricultural activities is observed in Belgium (Brulet, 1990). The Early Middle Ages were characterized by a more extended extractive industry and Pb-Zn ore extraction occurred (Dejonghe, 1998; Renson et al., 2005; see also Section 4.2.1). Further Si and Ti inputs to the bog are due to the extensive clearance and mining exploitation of sedimentary rocks, associated with the second industrial revolution.

#### 4.1.2. Chronological control

The chronology of the core is based on dates obtained from radiocarbon dating, palynology and  $^{210}\text{Pb}$ . Only one sample at 53.5 cm has been  $^{14}\text{C}$ dated. This gave an age of  $326 \pm 76$  cal A.D. (Late Roman Empire). The results of pollen profiles from previous studies in the same bog were used to delineate critical periods of human activities (Hindryckx, 2000; Hindryckx and Streel, 2000; Gérard, 2004; Goormaghtigh, 2005). All cores used for palynology were retrieved within 100 m of the core site used in this study, where peat thickness extended more than 6.5 m (see Fig. 1). In all pollen diagrams used, the top meter is representative of the young Subatlanticum Zone XI (as defined by Firbas, 1939), covering roughly the last 2000 years. This zone is characterized by abundant pollen maxima of *Fagus* (beech tree) and significant presence of *Carpinus* (hornbeam) (>1-2%). These palynological characteristics have been controlled in the present core by Gérard (2004) and Goormaghtigh (2005). Coincidence of abundant *Fagus* and start of *Carpinus* has been recently dated at 150 A.D. by Streel et al. (2006) in a peat bog a few kilometers to the South-East of the Misten bog. In the Misten bog, Hindryckx and Streel (2000) dated the third peak of *Fagus* at around  $1140 \pm 125$  A.D. This third maximum of *Fagus* is found at 30 cm depth in the present core (Goormaghtigh, 2005), providing a chronological indicator for the Middle Ages.

With the date of 150 A.D. around 95 cm depth (Streel et al., 2006), our new date of  $326 \pm 76$  A.D. at 53.5 cm, the date of  $1140 \pm 125$  A.D. (Hindryckx and Streel, 2000) around 30 cm depth, and finally our Pb age model for the subsurface, a rather accurate age-depth relationship can be accepted.

#### 4.1.3. Can Si and Ti measurements provide evidence for Roman activities?

Si and Ti increase significantly between 90 and 55 cm depth. It has already been shown that land clearance, farming, and following erosion could play a role in Si and Ti inputs to a peat bog (Holynska et al., 1998; Hölzer and Hölzer, 1998; Görres, 1993). An increase in Si and Ti often reflects an increase in soil dust inputs (e.g. Holynska et al., 1998; Shotyky et al., 1998; Görres, 1993). In support for this in our core, the cereal pollen content increase between 80 and 60 cm (Goormaghtigh, 2005), favoring the hypothesis of cultivation. Arkose mining and gold prospecting could also have played a role. However, with little known about the age of these mines, we conclude that it is most likely that the primary input of Si and Ti-bearing particle are due to extensive Roman agricultural activities.

## 4.2. Origin of heavy metals through the last 2000 years

The origin of lead and associated heavy metals can be established both by  $^{208}\text{Pb}/^{207}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  diagram and Pb E.F. coupled with  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratio (Fig. 5). The principle being the isotopic signature changes with origin of particles from the upper continental crust, through Belgian ores and toward a signature of modern Benelux aerosols (see Fig. 4 for references). The lowermost samples (660 cm and 678 cm) show good agreement with upper continental crust values (Millot et al., 2004; Hemming and McLennan, 2001; Grousset et al., 1994; Asmeron and Jacobsen, 1993) and Belgian pre-industrial background sediments from Sonke et al. (2002). However, the least radiogenic values of  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios are still far from The Netherlands gasoline (similar to Belgian gasoline) values ( $^{208}\text{Pb}/^{206}\text{Pb} = 2.28 \pm 0.013$ ,  $^{206}\text{Pb}/^{207}\text{Pb} = 1.062 \pm 0.019$ ) reported by Hopper et al. (1991).

### 4.2.1. Roman Empire

In the core Pb enrichment factors display a wide range of variation during the Early Roman Empire with isotopic ratios being very low (see Fig. 5, samples at 98.5 cm and 88.5 cm depth). During the Roman Empire, and particularly towards the upper end (60 cm-40 cm) Pb E.F. are quite high (up to 110) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio shows lower radiogenic values ( $^{206}\text{Pb}/^{207}\text{Pb}$  up to 1.154).

It is known that Romans mined and extracted a wide range of ores all over NW Europe and around the Mediterranean Sea, increasing significantly the amount of aerosol which has a wide range of Pb-isotopic composition particles in the air. However, in the Misten bog, it seems that a more local influence has been recorded. Indeed, the isotopic values of samples from 98.5 cm to 50 cm depth show good agreement with the isotopic field of the Belgian Pb-Zn ores (Fig. 4).

In Belgium, there is no historical, archaeological or field evidence for Roman Pb-Zn mining. However, Renson (2005) and Renson et al. (2007), in their study on a peat column taken nearby an archaeological site constituted by a Roman to Merovingian road in the Hautes Fagnes, found and dated very high Zn concentrations (up to 1000 ppm) associated with peaks in lead concentration (up to 80 ppm). Such high concentration clearly reflect a local pollution linked to the road (Renson, 2005). Moreover, the lead isotopic composition ( $^{208}\text{Pb}/^{207}\text{Pb} \sim 1.17-1.18$ ,  $^{208}\text{Pb}/^{206}\text{Pb} \sim 2.08-2.10$ ) of the Pb and Zn-contaminated levels found by Renson (2005) and Renson et al. (2007) are in very good agreement with isotopic composition of Pb-Zn ores located 15 km northwards to the Hautes Fagnes Plateau. These new data suggests that local Pb-Zn ores from the Verviers area (for location see Fig. 1.) were extracted and transported through the Hautes Fagnes Plateau from around A.D. 150 (Renson, 2005).

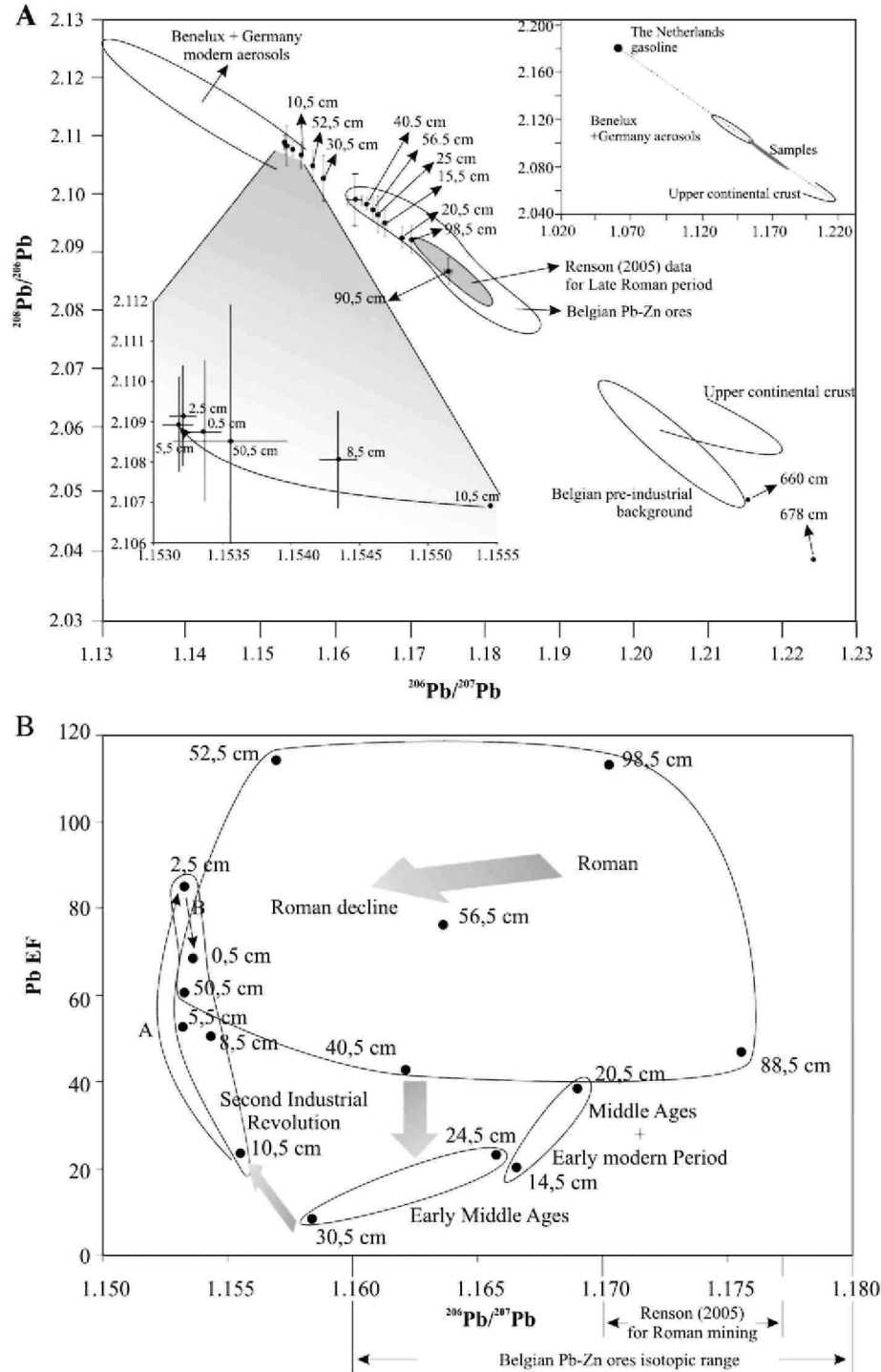
In conclusion, although there is no field archaeological evidence for Roman lead-zinc ore mining in Belgium, this study from this study and from Renson (2005) and Renson et al. (2007) show significant support for mining of Pb-Zn ores in Belgium during the Roman Empire.

### 4.2.2. Late Roman Empire and Early Middle Ages

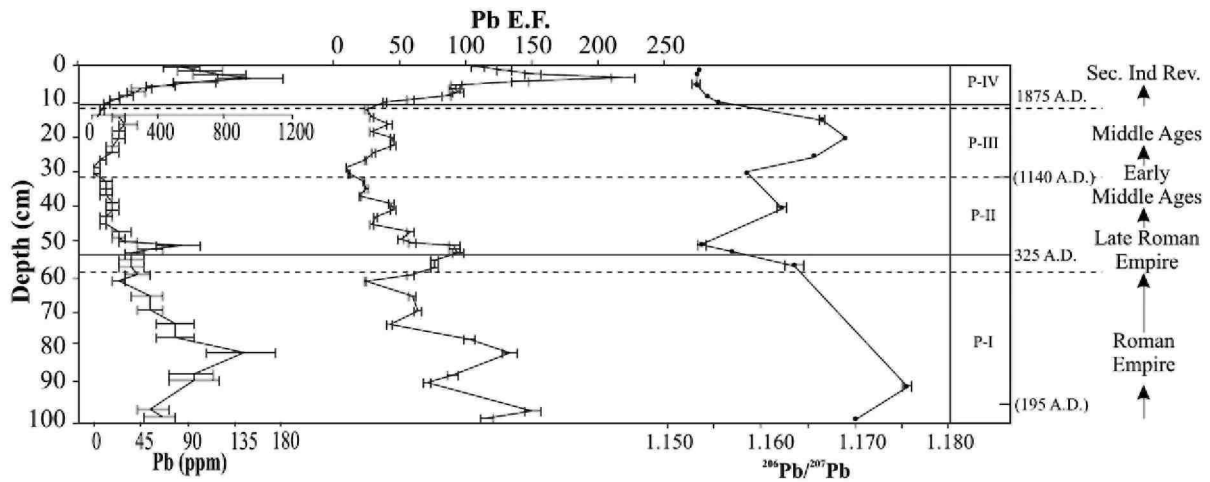
Following the Roman Empire, the next phase of change is characterized by a decrease in Pb enrichment factors ( $\sim 40$  cm-25 cm depth), reflecting the decline of the Roman mining activities. Minimum Pb E.F values (less than 20) are observed between depth of 35 cm and 25 cm. This Early Middle Ages period has already been well documented in other European peat bogs (e.g. Le Roux et al., 2004). Its main geochemical characteristic in peat bogs is a wide range of Pb isotopic composition, but low Pb E.F, as various ores were mined across Europe, but in smaller quantities, as suggested in the estimation from Settle and Patterson (1980) and the data from Hong et al. (1994). Here however, although mining industries were growing up across Europe, the most probable source of anthropogenic dust is the Belgian ore bodies (Fig. 4 above).

This period is followed by the Classic and Late Middle Ages (i.e. 900 A.D. to 1450 A.D.), and the Early modern period (i.e. 1450 A.D. to 1700 A.D.). This time period is represented by Pb isotopic signatures which also match well with Belgian ores. The extraction of these ores are well documented in historical texts back to Middle Ages (Dejonghe, 1998), adding a new source for Pb inputs to Belgian bogs.

**Fig. 4:**  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{208}\text{Pb}/^{206}\text{Pb}$  isotopic ratios, and  $^{206}\text{Pb}/^{207}\text{Pb}$  vs. Pb E.F. Modern industrial Belgian aerosols from Bollhöfer and Rosman (2001), and Sonke et al. (2002). Belgian ore data from Cauet et al. (1982) and Dejonghe (1998). Data from archeological site from Renson et al. (2007) are also reported. Belgian pre-industrial sediment from Sonke et al. (op. cit.). Upper continental crust field from Millot et al. (2004), Hemming and McLennan (2001), Grousset et al. (1994) and Asmeron and Jacobsen (1993). Gasoline from The Netherlands from Hopper et al. (1991).



**Fig. 5:** Summary of major Pb, Pb E.F. and  $^{206}\text{Pb}/^{207}\text{Pb}$  in the first meter Misten bog and interpretation of historical intervals. The x-scale of Pb profile has been changed at 15 cm depth for visual clarity.



#### 4.2.3. Industrial revolution

Between 10 cm (1835 A.D.) and 2.5 cm (1964 A.D.), Pb E.F. increase in parallel with a small decrease of Pb/Pb ratio. During this period enhanced local Pb-Zn ore processing (~1840 A.D., Dejonghe, 1998) together with coal mining and burning (Gaier, 1988), and the introduction of leaded gasoline, allow the addition of tremendous amounts of anthropogenic aerosols in the atmosphere. Around 1975, the estimated anthropogenic Pb was about 4240 metric tons per annum (p.a.) in Belgium, 2263 metric tons p.a. in The Netherlands, 18,860 metric tons p.a. in France, and 16,500 metric tons p.a. in nearby Germany (cumulated FDR and DDR, von Storch et al., 2003). This strong increase in atmospheric pollution is recorded in the Misten bog by a marked increase in Pb from 89.1 ppm at 10.5 cm to 949 ppm at 3.5 cm depth. This is followed by related heavy metals concentrations (from 10.5 cm to 3.5 cm depth, Cu from 1.8 ppm to 18.7 ppm, Ni from <D.L. to 22.8 ppm, Zn from 91.6 ppm to 214 ppm), together with an increase of Pb E.F. (from 39 to 218) and shifts in lead isotopic ratios ( $^{206}\text{Pb}/^{207}\text{Pb}_{15\text{ cm}} = 1.1666$ , then  $^{206}\text{Pb}/^{207}\text{Pb}_{2\text{ cm}} = 1.1532$ ). Reduced radiogenic Pb/Pb values do not, however, predate the maximum Pb concentrations and Pb E.F. as previously reported in peat cores from Denmark, Greenland (Shotyk et al., 2003) and the Faeroe Islands (Shotyk et al., 2005). Shotyk et al. (2003) argued that in Denmark or Greenland, this shift is linked to the predominance of coal burning more than the total Pb pollution. It is therefore likely that, in the Hautes Fagnes, leaded gasoline accounts at least as much as the other Pb sources (industries and coal burning) for the Pb input in this area. This is further corroborated by observations from von Storch et al. (2003), who reported that among the diverse anthropogenic Pb sources, leaded gasoline is the main one, increasing from its introduction (1931 A.D.) and reaching a maximum in the early 1970's. During this period, leaded gasoline accounted for 75% of the total atmospheric lead emission across Europe. In the same study, decadal estimations of anthropogenic Pb emissions over the last 50 years show a maximum around 1965, which also agrees with our findings.

#### 4.2.4. Unleaded gasoline

The phasing out of lead in gasoline began in 1972 in Europe. Indeed, during the European oil crisis, Germany began to adopt policies to reduce lead content of gasoline. This was followed by the first EU regulation (1981). Between 1984 and 1989, unleaded gasoline was progressively introduced across Europe. As a result, atmospheric Pb emissions began to decrease slightly in the second half of the 1960's, then suddenly by the mid-1970's (von Storch et al., 2003). Although there are slight discrepancies of age in our peat core due to sampling intervals (1 cm representing a mean of 20 years above 3 cm depth, see Table 2), this decrease in Pb concentration and Pb E.F. is marked in the upper samples from above 3.5 cm depth, and is therefore representative for post-A.D. 1950. These records also correspond with diverse records from Belgium (Petit et al., 1984), France (Rosman et al., 2000; Arnaud et al., 2004), and Switzerland (Kober et al., 1999; Shotyk et al., 1998).

## 5. Conclusions

Geochemical and lead isotopic derived from the top meter of peat from the Misten peat bog (Fig. 5) record four major periods of pollution. Firstly the Roman Empire (P-I), represented between 100 cm and ~ 57 cm, is

characterized by local pollution sources from Pb-Zn ores mining and agriculture activities. Between ~ 57 cm and ~ 30 cm, the geochemical profiles show a decline in the Roman activities and the transition to Early Middle Ages (P-II). The Middle Ages and Early modern period (~30 cm to ~10 cm, P-III) rapidly give way to the modern industrial Revolution (from ~10 cm to the actual surface, P-IV) in which lead gasoline accounts for at least 50% of the lead pollution.

This study provides the opportunity to complete the European datasets for pollution reconstruction in continental environments.

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