High-resolution reconstruction of atmospheric deposition of trace metals and metalloids since AD 1400 recorded by ombrotrophic peat cores in Hautes-Fagnes, Belgium
Mohammed Allan, Gaël Le Roux, François de Vleeschouwer, Richard Bindler, Maarten Blaauw, Natalia Piotrowska, Jaroslaw Sikorski, Nathalie Fagel

To cite this version:
Mohammed Allan, Gaël Le Roux, François de Vleeschouwer, Richard Bindler, Maarten Blaauw, et al.. High-resolution reconstruction of atmospheric deposition of trace metals and metalloids since AD 1400 recorded by ombrotrophic peat cores in Hautes-Fagnes, Belgium. Environmental Pollution, 2013, vol. 178, pp.381-394. 10.1016/j.envpol.2013.03.018. hal-00977497

HAL Id: hal-00977497
https://hal.science/hal-00977497
Submitted on 11 Apr 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.
Allan, Mohammed and Le Roux, Gaël and De Vleeschouwer, François and Bindler, Richard and Blaauw, Maarten and Piotrowska, Natalia and Sikorski, Jaroslaw and Fagel, Nathalie

High-resolution reconstruction of atmospheric deposition of trace metals and metalloids since AD 1400 recorded by ombrotrophic peat cores in Hautes-Fagnes, Belgium. (2013) Environmental Pollution, vol. 178 . pp. 381-394. ISSN 0269-7491
High-resolution reconstruction of atmospheric deposition of trace metals and metalloids since AD 1400 recorded by ombrotrophic peat cores in Hautes-Fagnes, Belgium

Mohammed Allan a,*, Gaël Le Roux b, c, François De Vleeschouwer b, c, Richard Bindler d, Maarten Blaauw e, Natalia Piotrowska f, Jaroslaw Sikorski f, Nathalie Fagel a

a AGES, Département de Géologie, Université de Liège, Allée du 6 Août, B18 Sart Tilman B-4000, Liège, Belgium
b Université de Toulouse, INP, UPS, Ecolab (Laboratoire Ecologie Fonctionnelle et Environnement), ENSAT, Avenue de l’Agrobiopole, 31326 Castanet Tolosan, France
c CNRS, Ecolab, 31326 Castanet Tolosan, France
d Department of Ecology and Environmental Science, Umeå University, KBC Building, 90187 Umeå, Sweden
e School of Geography, Archaeology & Palaeoecology, Queen’s University Belfast, UK
f Department of Radioisotopes, GADAM Centre of Excellence, Institute of Physics, Silesian University of Technology, Gliwice, Poland

Keywords: Atmospheric pollution
Industrial Revolution
Trace metals
Lead isotopes
Misten bog

A B S T R A C T

The objective of our study was to determine the trace metal accumulation rates in the Misten bog, Hautes-Fagnes, Belgium, and assess these in relation to established histories of atmospheric emissions from anthropogenic sources. To address these aims we analyzed trace metals and metalloids (Pb, Cu, Ni, As, Sb, Cr, Co, V, Cd and Zn), as well as Pb isotopes, using XRF, Q-ICP-MS and MC-ICP-MS, respectively in two 40-cm peat sections, spanning the last 600 yr. The temporal increase of metal fluxes from the inception of the Industrial Revolution to the present varies by a factor of 5–50, with peak values found between AD 1930 and 1990. A cluster analysis combined with Pb isotopic composition allows the identification of the main sources of Pb and by inference of the other metals, which indicates that coal consumption and metallurgical activities were the predominant sources of pollution during the last 600 years.

1. Introduction

Trace metals and metalloids (referred here as trace metals) have been dispersed into the environment by human activities since the beginning of metallurgy (Nriagu, 1996). The increased in atmospheric deposition of trace metals compared to prehistoric levels is marked in the northern Hemisphere, particularly in Europe since at least 2000 years (Renberg et al., 1994; Hong et al., 1994). Mining and metallurgical activities, and later also coal burning and transport emissions were the principal anthropogenic sources (Nriagu, 1979; Pacyna and Pacyna, 2001; Pacyna et al., 2007; Shotyk and Le Roux, 2005). At present, soil contamination by atmospheric deposition can be expressed as a sum of local contamination by past and on-going human activities and by long-range atmospheric transport of trace metals. The magnitude and timing of changes in atmospheric trace metals deposition have been studied in a variety of environmental archives. Peat records from ombrotrophic bogs can provide valuable information about the atmospheric inputs of trace metals (e.g., Shotyk et al., 1996; Martinez-Cortizas et al., 1997; Farmer et al., 2009), because they are fed with nutrients and pollutants only through atmospheric inputs. Ombrotrophic peatlands could also store a faithful signal (i.e. no significant post-depositional remobilization) of the changing deposition, and thus of the content of elements/compounds in the atmosphere (Gore, 1983; Damman, 1986; Shotyk et al., 2001, 2002).

The evolution of the current accumulation of heavy metals in the environment my help to establish the magnitude and nature of the anthropogenic sources. Records of trace metals in bogs indicate that the Industrial Revolution marked a time of enhanced atmospheric pollution, caused by mining, fossil fuel combustion, agriculture, industry, urban development, and vehicle traffic (e.g., Martinez-Cortizas et al., 1997; Shotyk et al., 1998; De Vleeschouwer et al., 2009). To assess the extent of atmospheric contamination, it is necessary to identify the main past and present sources of trace metal emissions.
Not only atmospheric deposition of trace metals with established environmental concern, such as cadmium, lead and mercury (Pontevedra-Pombal et al., 2013), should be investigated, but also other metals with recent increased use and emission such as antimony (Shotyk et al., 2005a).

The mobility of metal and metalloid elements may be due to various factors such as adsorption on oxy-hydroxides and variations in pH (e.g., Rausch et al., 2005a,b), or uptake and recycling by plants (e.g., Damman, 1978; MacKenzie et al., 1998). Numerous studies demonstrated that Pb is an immobile element in ombrotrophic bog based on stable and radioactive Pb isotopes, Pb profiles in porewaters comparison with rain collectors and herbarium samples and transplant experiments (e.g. Shotyk et al., 2001; Weiss et al., 2002; Farmer et al., 2005; Livett et al., 1979; Novak and Pacherova, 2005). However, some investigations also demonstrated that Pb can be affected by diagenetic remobilization and redistribution processes in saturated peats (e.g., MacKenzie et al., 1998; Ollid et al., 2010). Zinc is often associated to Pb in sulfide minerals (including galena) and coals (Shotyk et al., 2003, 2005). However, Zn behavior is different to that of Pb in ombrotrophic bog. In contrast to the immobility of Pb, Zn can be mobile due to bioaccumulation, redistribution by plants, and pH conditions (Damman, 1978; Kemper and Frenzel, 1999; Livett et al., 1979; Novak and Pacherova, 2008). Rausch et al. (2005a,b) studied three peat cores from Finnish bogs and found that Cd is mobile after post-depositional processes, while Co was immobile. Compared to Pb and Zn, Cu has been less studied in ombrotrophic bog. Niemann et al. (2002) showed that Cu could be preserved in a peat record in close proximity to a major smelter, whereas Shotyk et al. (2002) and Ukonmaanaho et al. (2004) found that Cu could be affected to some extent by plant uptake like Zn. Rausch et al. (2005a,b) suggested that the pH and mineralogy controlled the Cu mobility in peat. Recently, Novak et al. (2011) demonstrated that Pb, Cu and Zn were immobile in two peat cores collected in the Czech Republic.

2.2. Elemental geochemistry and Pb isotope analyses

Because the two cores were initially part of two different studies, the samples from each one were analyzed separately using different methods.

2.2.1. MIS-08-01W core

Peb samples were digested by microwave autoclave at the Institute of Earth Sciences (University of Heidelberg) using a mixture of HNO$_3$ (3 ml) and HBF$_4$ (0.1 ml) according to Krachler et al. (2002). The digestion of organic matter was improved by an addition of H$_2$O$_2$ in the reaction chamber (Krachler et al., 2002). After digestion, ~3 ml of solution were poured into a Falcon tube and filled up to 14 ml. A fresh aliquot was used to measure the concentrations of trace elements, as well as lithogenic and conservative elements Al, Sc, and Ti. These elements were measured by Quadrapole Inductively Coupled Plasma Mass Spectroscopy (Q-ICP-MS, 7500 ce. Agilent Technologies), at the Observatoire Midi-Pyrénées, Toulouse, France, after adequate dilution and spiking with a standard In-Re for internal normalizers and procedural processes. Three certified reference materials (ICP-MS CTA-OTL-1 Oriental Tobacco Leaves, NIST Tomato Leaves 1573 and IEA Lichen 136) were analyzed with each series of samples, in order to determine the precision and accuracy of analytical procedures. Comparison between reference values and measured values were satisfactory (Table 1) within 88–97%. For V, Cr, Co, Ni, Cu, Zn, As, Pb and Cd, the reproducibility was higher than 92%. The lowest value was observed for Sb (87% for Tobacco leaves CTA-OTL standard).

A second aliquot was used to measure the Pb isotopic composition (Table 2). The dried samples were dissolved in a mixture of concentrated HNO$_3$ and HF in a proportion of 1:4 and heated at 125 °C for 2 h. After drying, 2 ml of 6M HCl were added to ensure complete digestion and the solutions were evaporated. For separation of Pb isotopes andREE (e.g., La, Ce, Nd, Nd), the samples were dissolved in 0.5 ml of 0.8 M 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, Université Libre de Bruxelles. The mass fractionation was internally corrected for mass bias using the known $^{205}$Pb/$^{204}$Pb ratio (Thirwall, 2002). 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 three analysis sessions [n = 41, $^{206}$Pb/$^{204}$Pb = 19.1673 ± 0.0032 (2σ), $^{207}$Pb/$^{204}$Pb = 15.4958 ± 0.0044 (2σ)]. Pb/NBS981 values are in agreement with the long-term laboratory value [n = 1000, $^{206}$Pb/$^{204}$Pb = 19.1503 ± 0.0012 (2σ), $^{207}$Pb/$^{204}$Pb = 15.4953 ± 0.0004 (2σ)]. Pb/NBS981 and Pb/NBS981 ratios are comparable to the Pb/NBS981 values reported in the literature (e.g., Benson et al., 2008; Galer and Abochami, 1998).

2.2.2. MIS-08-06W core

The concentrations of selected major and trace elements (Al, Ti, Ni, Cu, Zn, Pb) were measured on 2 g of dried and homogenized powder using a Bruker S8 TIGER wavelength-dispersive X-Ray Fluorescence (WD-XRF) analyzer equipped with an Rh anticathode X-ray tube. Powders were transferred in 40-mm opening plastic cups with a 2.5-μm Mylar film at the base. After that they were placed in metallic cup holders for analysis using a 34 mm mask. A specific calibration was developed in order to optimize the WD-XRF for the matrices of the samples (De Vleeschouwer et al., 2013). This was achieved using 27 certified reference materials, consisting of tree and vegetable leaves (NIST1515, NIST1547, NIST1570a, NIST1573a, BCR62, NIES1, NIES7), pine needles (NIST1575a), wheat flour (NIST4837, NIST4838), rice flour (NIES10a, NIES10b, NIES10c), lichen (BCR482), aquatic plants (BCR60, NIES3, NIES5), peat (NMF-UOE-FM-001, NP942-1), wood (NP943-3), hay powder (BCR120), milk...
powder (BCR150), coal (NIST1632b, NIST1635, SARM20), coke (NIST2718) and vehicle exhaust particles (NIES8). This selection is based on the certified values available in each CRM, which are matched with the expected detectable concentrations of our WD-XRF spectrometer. The last 3 CRM categories were included to extend the range of various trace elements. An internal standard was measured daily to check the analytical performance of the XRF. Three additional internal standards were used to monitor the long-term (yearly) drift of the device and to correct intensities if necessary. Results, as well as detection limits and standard deviations are reported in Table 3.

2.3. Chronology

For both cores, radiocarbon ages (5 samples for 01W and 22 samples for 06W) were obtained on aboveground plant macrofossils extracted following the methods described in Kilian et al. (1995) and Mauquoy et al. (2004). Samples were purified and graphitized prior to Acceleration Mass Spectrometry (AMS) measurement, at the GADAM Center for Excellence (University of Gliwice, Poland) following the protocol defined by Pietrowoska et al. (2010, 2011). 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 (2008) and De Vleeschouwer et al. (2010b). The $^{14}$C and $^{210}$Pb data and the age model for core 01W are reported in Allan et al. (2012), while the age model of 06W is reported in De Vleeschouwer et al. (2012). We used the Bacon age-depth modeling routines (Blaauw and Christen, 2011) to establish a coherent evolution of deposition along the core depth, and possibly including some sections where discontinuities are suspected (hiatuses). In this paper, we apply these age models to plot proxy vs. depth diagrams (Figs. 2, 4), where the calendar scale uncertainties are also indicated using gray-scales. The age-depth models show that peat accumulation is non-linear. Moreover, peat profiles which are situated close together, such as 01W and 06W, may exhibit very different growth rates. Regarding the last 600 years, the mean peat accumulation rate varies between 0.02 and 0.09 cm yr$^{-1}$ for 01W (from 40 to 17 cm), and for 06W between 0.03 and 0.08 (from 40 to 10 cm). Above 17 cm for 01W and 10 cm for 06W, and until the top, the accumulation rate increases drastically (AR 0.1–1.3) and marks the progressive shift from the catotelm to the acrotelm, characterized by living plants and uncompressed peat. The section of each of the two peat cores studied in further detail here span the period from ca. AD 1400 to the present.

2.4. Calculation of enrichment factors

The variation in trace metal concentrations can be explained by changes in supply, changes in their origin (natural or anthropogenic sources), and 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 matter is to calculate an enrichment factor for each metal by using a conservative element indicative of mineral matter, such as Ti. Mineral contribution to the bogs

![Fig. 1. Map of the Misten bog modified from De Vleeschouwer et al. (2007). The color indicates the peat thickness deduced from surface radar prospection (Wastiaux and Schumacker, 2003). The red dot indicates the location of cores MIS-08-01W (01W, this study) and MIS-08-06W (06W, De Vleeschouwer et al., 2012). The blue dot indicates the location of a core previously investigated by De Vleeschouwer et al. (2007). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
Table 2
Pb isotopic ratios measured by MC-ICP-MS Nu Plasma and standard deviations.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>(^{208}\text{Pb}/^{206}\text{Pb})</th>
<th>(2\sigma)</th>
<th>(^{208}\text{Pb}/^{206}\text{Pb})</th>
<th>(2\sigma)</th>
<th>(^{206}\text{Pb}/^{204}\text{Pb})</th>
<th>(2\sigma)</th>
<th>(^{206}\text{Pb}/^{204}\text{Pb})</th>
<th>(2\sigma)</th>
<th>(^{206}\text{Pb}/^{204}\text{Pb})</th>
<th>(2\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>38.00507</td>
<td>0.00252</td>
<td>15.6367</td>
<td>0.00095</td>
<td>18.29126</td>
<td>0.00105</td>
<td>2.07783</td>
<td>0.00044</td>
<td>1.16977</td>
<td>0.00012</td>
</tr>
<tr>
<td>6.5</td>
<td>37.89126</td>
<td>0.00216</td>
<td>15.6251</td>
<td>0.00086</td>
<td>18.18608</td>
<td>0.00095</td>
<td>2.08356</td>
<td>0.00034</td>
<td>1.16388</td>
<td>0.00012</td>
</tr>
<tr>
<td>10.1</td>
<td>37.87916</td>
<td>0.002</td>
<td>15.6045</td>
<td>0.00077</td>
<td>18.08185</td>
<td>0.00087</td>
<td>2.10232</td>
<td>0.00038</td>
<td>1.15466</td>
<td>0.00014</td>
</tr>
<tr>
<td>11.9</td>
<td>37.88852</td>
<td>0.00117</td>
<td>15.5921</td>
<td>0.00036</td>
<td>17.95033</td>
<td>0.00094</td>
<td>2.11073</td>
<td>0.00046</td>
<td>1.15125</td>
<td>0.00013</td>
</tr>
<tr>
<td>13.7</td>
<td>37.89525</td>
<td>0.00218</td>
<td>15.5935</td>
<td>0.00089</td>
<td>17.93328</td>
<td>0.00107</td>
<td>2.11075</td>
<td>0.00041</td>
<td>1.15133</td>
<td>0.00012</td>
</tr>
<tr>
<td>17.3</td>
<td>37.70398</td>
<td>0.00386</td>
<td>15.5817</td>
<td>0.00169</td>
<td>17.8752</td>
<td>0.00188</td>
<td>2.09311</td>
<td>0.00042</td>
<td>1.14679</td>
<td>0.00016</td>
</tr>
<tr>
<td>19.1</td>
<td>37.99162</td>
<td>0.00214</td>
<td>15.5997</td>
<td>0.00073</td>
<td>18.02459</td>
<td>0.00082</td>
<td>2.10773</td>
<td>0.00041</td>
<td>1.15546</td>
<td>0.00014</td>
</tr>
<tr>
<td>22.7</td>
<td>38.22536</td>
<td>0.00204</td>
<td>15.6153</td>
<td>0.00079</td>
<td>18.23794</td>
<td>0.00091</td>
<td>2.09592</td>
<td>0.00041</td>
<td>1.16796</td>
<td>0.00013</td>
</tr>
<tr>
<td>25.6</td>
<td>38.19245</td>
<td>0.00151</td>
<td>15.6147</td>
<td>0.00057</td>
<td>18.20114</td>
<td>0.00069</td>
<td>2.09841</td>
<td>0.00047</td>
<td>1.16564</td>
<td>0.00012</td>
</tr>
<tr>
<td>26.5</td>
<td>38.28559</td>
<td>0.00206</td>
<td>15.6180</td>
<td>0.00079</td>
<td>18.30171</td>
<td>0.00085</td>
<td>2.10232</td>
<td>0.00038</td>
<td>1.15466</td>
<td>0.00013</td>
</tr>
<tr>
<td>28.6</td>
<td>38.34574</td>
<td>0.00216</td>
<td>15.6209</td>
<td>0.00084</td>
<td>18.36624</td>
<td>0.00093</td>
<td>2.08791</td>
<td>0.00046</td>
<td>1.17571</td>
<td>0.00014</td>
</tr>
<tr>
<td>30.6</td>
<td>38.35816</td>
<td>0.00193</td>
<td>15.6177</td>
<td>0.00084</td>
<td>18.38396</td>
<td>0.00099</td>
<td>2.08651</td>
<td>0.00039</td>
<td>1.17711</td>
<td>0.00012</td>
</tr>
<tr>
<td>40.6</td>
<td>38.37774</td>
<td>0.00223</td>
<td>15.6214</td>
<td>0.00088</td>
<td>18.39727</td>
<td>0.00084</td>
<td>2.08599</td>
<td>0.00041</td>
<td>1.17768</td>
<td>0.00012</td>
</tr>
</tbody>
</table>

Table 3
Statistics on XRF data used for core 06W. The number of certified reference material varies because not all the CRM are certified for the selected elements. Reproducibility values are the median values of 10 measurements performed on 3 certified reference materials: NIMT-UOE-FM-001, NVJ-94-2 and NST-1515.

| Element | Na | Mg | K | Ca | Al | Si | Ti | Fe | Mn | Ba | Rb | Sr | S | P | Cl | Br | Cu | Zn | Pb | Ni |
|---------|----|----|---|----|----|----|----|----|----|----|----|----|---|---|---|----|----|----|----|----|----|
| Number of CRM | 13 | 16 | 19 | 19 | 17 | 8  | 8  | 16 | 22 | 5  | 10 | 10 | 12 | 12 | 7  | 24 | 9  | 12 |
| LLD (\(\mu g\ \text{g}^{-1}\)) | 20 | 16 | 7  | 6  | 3  | 16 | 2  | 9  | 1  | 54 | 1  | 1  | 8  | 10 | 7  | 0.4| 0.5| 2  | 0.5|
| Accuracy (%) | 8 | 6  | 7  | 5  | 9  | 19 | 11 | 12 | 4  | 4  | 11 | 17 | 10 | 6  | 6  | 7  | 10 | 8  | 12 | 9  |
| Reproducibility (%) | 78 | 98 | 97 | 99 | 98 | 95 | 98 | 97 | 97 | 53 | 93 | 98 | 99 | 97 | 99 | 92 | 88 | 98 | 92 | 77 |
Fig. 2. Major and trace element concentration (µg g⁻¹) and Pb isotope ratios versus depth in both 01W (black line) and 06W (gray line) cores.

Fig. 3. Enrichment factors (EF) in both cores 01W and 06W. The EF has been normalized to the average concentration measured in basal layers of the profile (unpublished data), using Ti as reference element.
Fig. 4. a: Calculated total atmospheric AR (in mg m$^{-2}$ yr$^{-1}$) of Pb, Cu, Sb, As, V, Co, Cd and Zn for the core 01W. Calculated fluxes depend on element concentrations, modeled calendar ages and corresponding accumulation rates (based on the age-depth model provided by Bacon [Blaauw and Christen, 2011]). Darker gray indicates more likely values. b: Calculated total atmospheric AR (in mg m$^{-2}$ yr$^{-1}$) of Pb, Cu, Ni, As, Cr, V and Zn for the core 06W.
anthropogenic-derived contributions. In the Misten bog records (Fig. 3), EF are the most pronounced for Pb and Sb with maximum EF values >40, followed by Cd (>30). Copper, Ni, V, Co, Cr, Zn, and As are characterized by EF values averaging ~2–3 times the background values at the base of the peat sequence. Then EF values increase and reach a maximum between AD 1930 and 2000. In both cores, EF values of all trace metals (except Cd and Zn) remain stable from AD 1400 to 1700. The relative increase in EF is not the same for the metals from AD 1700 to 2000. EF increases by a factor of 10–20 (2.5–50 for 01W, 2.6 to 20 for 06W). EF increases by a factor of 50–70 (0.05–2.5 for 01W, 0.07 to 4.5 for 06W). EF increases in core 01W increases by a factor of 20, from 1 at 1700 to 22–40 at AD 1930–1991. EF increases by a factor of 5–30, from 0.04 to 1.2 for 01W and from 0.06 to 0.3 for 06W. EF increases by a factor of 10, from 0.35 (between AD 1700 and 1983–1991). EF increases by a factor of 10–30 between AD 1700 and 2000 in both cores. EF increases by a factor >100 between AD 1700 and 1995 in the core 01W. EF increases by a factor of 10–20, from 0.2 to 2.2 for 01W and from 0.3 to 6 for 06W. EF increases by a factor of 5–15 from ca. AD 1700 to 2000. EF increases by a factor of 30 from ca. AD 1700 to 2000 in core 01W. All EF values decrease toward the surface.

3.3. Lead isotope ratios

Table 2 summarizes results of Pb isotope analyses. In core 01W (Table 2), $^{208}$Pb/$^{204}$Pb, $^{207}$Pb/$^{206}$Pb and $^{206}$Pb/$^{208}$Pb isotopic ratios decrease from 40.6 cm (respectively, 38.3777 ± 0.0023, 16.6215 ± 0.0008 and 18.3973 ± 0.0008) to 17.3 cm (respectively, 37.7039 ± 0.0039, 15.5872 ± 0.0017 and 17.8752 ± 0.0019). From 13.7 cm to the surface of bog, the values of Pb isotope ratios show an increase (respectively, between 39.8752 ± 0.0022 and 38.0051 ± 0.0025, between 15.59218 ± 0.0009 and 15.6364 ± 0.0009 and between 17.9533 ± 0.0011 and 18.29126 ± 0.001).

3.4. Trace metals accumulation rates

In order to examine the historical record of pollution, we calculated the total accumulation rate (AR) of the trace metals in both cores (Fig. 4). Pre-anthropogenic AR for the trace metals were measured in the deepest peat layers (from 600 to 750 cm, n = 45) (Pb AR = 0.15 mg m⁻² yr⁻¹, Cu AR = 0.18 mg m⁻² yr⁻¹, Sb AR = 0.003 mg m⁻² yr⁻¹, Ni AR = 0.22 mg m⁻² yr⁻¹, As AR = 0.002 mg m⁻² yr⁻¹, Cr AR = 0.12 mg m⁻² yr⁻¹, V AR = 0.06 mg m⁻² yr⁻¹, Co AR = 0.11 mg m⁻² yr⁻¹, Cd AR = 0.02 mg m⁻² yr⁻¹, and Zn AR = 2 mg m⁻² yr⁻¹). They are by far lower than the accumulation rates in the recent peat layers. The Pb AR remained lower than 2 mg m⁻² yr⁻¹ before the 17th century. The Pb AR increases from AD 1690 up to a maximum >100 mg m⁻² yr⁻¹ at AD 1937 for 06W and at AD 1990 for 01W. Since then the Pb AR has decreased to 4 and 0.2 mg m⁻² yr⁻¹ (respectively) at the surface in both cores (01W and 06W).

The AR of V, Cr, Co, Ni, Cu, As and Sb remained stable and lower in the lower part of the core between AD 1350 and 1690 (from 40 to 30 cm). The maximum AR is observed between AD 1930 and 1995 for all trace metals (Fig. 4). The relative increase in accumulation rates is not the same for the metals for the period (AD 1750 to AD 1980–1990):

- Copper AR increases by a factor of 15–50 (0.3–7 mg m⁻² yr⁻¹ for 01W, 0.1–3 for 06W) between AD 1750 and 1980–1990;
- Antimony AR in core 01W increases by a factor of 50, from 0.04 mg m⁻² yr⁻¹ at 1750 to ~2 mg m⁻² yr⁻¹ at AD 1983–1991;
- Nickel AR increases by a factor of 25–50, from 0.08 to 3 mg m⁻² yr⁻¹ for both cores, during the same time interval;
- Arsenic AR increases by a factor of 5, from 0.5 to 2.5 mg m⁻² yr⁻¹ (between AD 1750 and 1983–1991);
- Chromium AR increases by a factor of 25–30 between AD 1750 and 1980–1990 in both cores;
- Cobalt AR increases by a factor of 25–30 between AD 1750 and 1980–1990 in the core 01W;
- Vanadium AR increases by a factor of 25–30, from 0.1 to 6 mg m⁻² yr⁻¹ for both cores, during the same time interval;
- Zinc AR increases by a factor of 5–50 from ca. AD 1750 to 1995 in both cores;
- Cadmium AR increases by a factor of 5–50 from ca. AD 1750 to 1995 in core 01W.

3.5. Cumulative inventories of trace metals

We also investigated the variability of the total cumulative inventories of different trace elements (Table 3) considering the two peat cores and the depth until no unsupported $^{210}$Pb can be detected (Le Roux et al., 2005). The $^{210}$Pb inventories of the two cores, respectively 6.7 kBq m⁻² for 01W and 4.3 kBq m⁻² for 06W (De Vleeschouwer et al., 2010a), are in agreement with what can be expected (Le Roux and Marshall, 2011) considering the average annual rainfall in this area (~1400 mm). The higher inventory (56% higher) for $^{210}$Pb in the hummock core (01W) as compared to the hummock-hollow transition core (06W) was also found for Pb (70%), Cu (26%), V (33%), and Ni (34%) and to a lesser extent for Cr (16%) and Zn (7%). In contrast to the trace metals, lithogenic elements (Al, Ti) have lower inventories in 01W than in 06W. In order to understand these discrepancies, we also calculated the inventories of pollen grains from a palynological investigation on the same two cores (De Vleeschouwer et al., 2010c). Table 4 shows both the inventories of major pollen types as well as the typical average size of the pollen grains. The pollen grains have a larger size than the average atmospheric particles transporting trace metals (Allen et al., 2001; Baeyens and Dedeeuwaerder, 1991; Injuk et al., 1992), which are mainly transported by submicronic aerosols. A large part of the lithogenic elements are deposited as large atmospheric particles derived from local transport. The pollen inventories show that there is a good agreement between the two cores, except for Pinus and Quercus pollen, which is known to be long-range transported and thus possibly affected by atmospheric processes similar to submicronic aerosols (Allen et al., 2001). Bog pollen grains such as of Betula also show good agreement. The differences between the

<table>
<thead>
<tr>
<th>Pollen grains cm⁻²</th>
<th>Pinus (d ~ 100 μm)</th>
<th>Quercus (30 μm)</th>
<th>Betula (20-30 μm)</th>
<th>Pinus (75 μm)</th>
<th>Fagus (50 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01W</td>
<td>91.317</td>
<td>41.176</td>
<td>73.431</td>
<td>66.535</td>
<td>29.340</td>
</tr>
<tr>
<td>06W</td>
<td>98.057</td>
<td>56.953</td>
<td>85.126</td>
<td>49.381</td>
<td>29.636</td>
</tr>
</tbody>
</table>

Table 4
Cumulative inventories of $^{210}$Pb, Pb, Zn, Cu, V, Ni, Cr, Al, and Ti for Misten peat cores (01W and 06W).
lithogenic elements (Al, Ti) tracing large particles, trace elements carried by submicronic particles and pollen rain can be explained by different processes at the air-peat ground interface. At Misten bog, in a large open area, the differences can be mainly explained by differences in microtopography, affecting movements of particles and snow during winter. These movements are more susceptible to affect long-range transport particles emitted all year around or even more in winter due to domestic fuel consumption than pollen grains or large particles emitted during spring and summer. The minor remaining discrepancies in the cumulative inventories values of different trace elements between 01W and 06W are explained by the position of the coring itself. 01W core was taken on a hummock, while 06W core was taken between a hummock and a hollow (to record a maximum of wetness changes, according to De Vleeschouwer et al., 2010a,b; Aaby, 1976).

4. Discussion

4.1. Trace metal and metalloid mobility

One aim of this study was to assess the possible post-depositional mobility of trace metals in peat cores before interpreting the accumulation rates as quantitative records of past atmospheric deposition. This is especially critical when dealing with high-resolution records of fresh, poorly decomposed peat accumulating in the acrotelm.

In both the 01W and 06W cores, we suggest that most of the trace metals (V, Cr, Co, Ni, Cu, As, Pb and Sb) are largely immobile in the upper part of the Misten bog for two reasons. First, the timing of the maximum concentration and accumulation rate of Pb is consistent between the two cores from different settings on the bog, and with that in other European peat bogs (e.g., Shotyk et al., 1996, 1998, 2002; Cloy et al., 2005; Olid et al., 2010), and with records based on herbarium collections (Bacon et al., 1996; Weiss et al., 1999; Farmer et al., 2002) and lake sediments (e.g. Renberg et al., 2001). Moreover, in the Misten bog record there is a consistency among the concentration profiles of Cu, V, Ni and Cr and that for Pb (Fig. 2, 3; Table 5). Lead positively correlated with all metals studied along the both cores (Table 5).

Second, preservation of the atmospheric record is indicated by the comparison between V, Cr, Ni, Cu and Pb concentrations in 01W and 06W cores (Fig. 2). This comparison shows that maximum concentrations are between 18 and 22 cm-depth for 01W and between 10 and 14 cm-depth for 06W, but the change in their concentrations are similar in time (Fig. 2). This difference in concentration values between 01W and 06W are explained by the position of the coring itself. 01W core was taken on a hummock, while 06W core was taken between a hummock and a hollow, where hummocks are known to have higher interception of trace metals (Dammann, 1978; Oldfield et al., 1995; Norton et al., 1998) (see discussion below). The similar chronologies of some trace metals profiles in 01W and 06W peat sites with different characteristics and with different peat accumulation rates suggest that these records are preserved in the Misten bog deposit.

4.2. Trace metal sources

4.2.1. Pb isotope

Lead isotope ratios of peat samples allow the identification of the natural and anthropogenic sources of Pb, because many sources of Pb are characterized by different isotope ratios (e.g., Shirahata et al., 1980). In the binary diagram $^{206}$Pb/$^{204}$Pb vs. $^{208}$Pb/$^{204}$Pb, most of the 01W core data plot between the isotope field defined by Belgian ores, Belgian Zn-smelter, and Benelux urban aerosols measured during the leaded gasoline era (Fig. 5a). Eifel ores (Durali-Mueller et al., 2007), Belgian Pb—Zn ores (Cauet and Herbosh, 1982, Dejonghe, 1998) Benelux and Germany aerosol (Bollhöfer and Rosman, 2001) define a mixing line on which many of the samples lie. Lead isotope ratios measured in samples dated between AD 1690 and 1953 correspond to the isotopic fields of the Pb—Zn ores of the Verviers syncline and the Eifel ores (Durali-Mueller et al., 2007). The sample located in the upper part of the core (AD 1699–1777) has isotope ratios nearest to the values of the Belgian Zn-smelter (Sonk et al., 2002) and Benelux aerosols (Bollhöfer and Rosman, 2001). Our results are consistent with those obtained by De Vleeschouwer et al. (2007) in a former core recovered in the Misten bog (Fig. 5a).

The recent samples (from AD 1994 to 2007) do not lie on the mixing line between the two identified potential sources (i.e., Belgian ores and Benelux aerosols; Fig. 5a). Their $^{206}$Pb/$^{207}$Pb ratios, which vary from 1.147 to 1.169, are aligned along a second linear trend. This second trend was previously mentioned by Véron et al.

Table 5

Pearson correlation coefficients between metal concentrations in both cores, significant correlations in bold (r value).

<table>
<thead>
<tr>
<th>Core 01W</th>
<th>Al</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Cd</th>
<th>Sb</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1</td>
<td>0.92</td>
<td>0.90</td>
<td>0.61</td>
<td>0.56</td>
<td>0.69</td>
<td>0.53</td>
<td>0.45</td>
<td>0.41</td>
<td>0.77</td>
<td>0.20</td>
<td>0.57</td>
<td>0.62</td>
</tr>
<tr>
<td>Sc</td>
<td>0.92</td>
<td>1</td>
<td>0.86</td>
<td>0.79</td>
<td>0.73</td>
<td>0.80</td>
<td>0.73</td>
<td>0.70</td>
<td>0.70</td>
<td>0.23</td>
<td>0.22</td>
<td>0.63</td>
<td>0.75</td>
</tr>
<tr>
<td>Ti</td>
<td>0.90</td>
<td>0.86</td>
<td>1</td>
<td>0.71</td>
<td>0.66</td>
<td>0.76</td>
<td>0.61</td>
<td>0.58</td>
<td>0.59</td>
<td>0.33</td>
<td>0.05</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>V</td>
<td>0.61</td>
<td>0.79</td>
<td>0.71</td>
<td>1</td>
<td>0.95</td>
<td>0.95</td>
<td>0.96</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>Cr</td>
<td>0.56</td>
<td>0.73</td>
<td>0.66</td>
<td>0.96</td>
<td>1</td>
<td>0.86</td>
<td>0.97</td>
<td>0.89</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Co</td>
<td>0.69</td>
<td>0.83</td>
<td>0.76</td>
<td>0.95</td>
<td>0.86</td>
<td>1</td>
<td>0.91</td>
<td>0.92</td>
<td>0.94</td>
<td>0.81</td>
<td>0.21</td>
<td>0.66</td>
<td>0.68</td>
</tr>
<tr>
<td>Ni</td>
<td>0.53</td>
<td>0.73</td>
<td>0.61</td>
<td>0.98</td>
<td>0.97</td>
<td>0.91</td>
<td>1</td>
<td>0.95</td>
<td>0.19</td>
<td>0.63</td>
<td>0.01</td>
<td>0.81</td>
<td>0.70</td>
</tr>
<tr>
<td>Cu</td>
<td>0.45</td>
<td>0.63</td>
<td>0.58</td>
<td>0.95</td>
<td>0.89</td>
<td>0.92</td>
<td>0.95</td>
<td>1</td>
<td>0.20</td>
<td>0.65</td>
<td>0.02</td>
<td>0.87</td>
<td>0.76</td>
</tr>
<tr>
<td>Zn</td>
<td>0.41</td>
<td>0.42</td>
<td>0.29</td>
<td>0.20</td>
<td>0.06</td>
<td>0.44</td>
<td>0.19</td>
<td>0.20</td>
<td>1</td>
<td>0.66</td>
<td>0.90</td>
<td>0.26</td>
<td>0.47</td>
</tr>
<tr>
<td>As</td>
<td>0.77</td>
<td>0.78</td>
<td>0.73</td>
<td>0.67</td>
<td>0.55</td>
<td>0.81</td>
<td>0.63</td>
<td>0.65</td>
<td>0.66</td>
<td>1</td>
<td>0.45</td>
<td>0.81</td>
<td>0.92</td>
</tr>
<tr>
<td>Cd</td>
<td>0.20</td>
<td>0.22</td>
<td>0.05</td>
<td>0.03</td>
<td>0.21</td>
<td>0.21</td>
<td>0.01</td>
<td>0.02</td>
<td>0.90</td>
<td>0.45</td>
<td>1</td>
<td>0.02</td>
<td>0.23</td>
</tr>
<tr>
<td>Sb</td>
<td>0.57</td>
<td>0.64</td>
<td>0.70</td>
<td>0.84</td>
<td>0.76</td>
<td>0.88</td>
<td>0.81</td>
<td>0.87</td>
<td>0.86</td>
<td>0.81</td>
<td>0.02</td>
<td>1</td>
<td>0.94</td>
</tr>
<tr>
<td>Pb</td>
<td>0.62</td>
<td>0.68</td>
<td>0.70</td>
<td>0.75</td>
<td>0.61</td>
<td>0.85</td>
<td>0.70</td>
<td>0.76</td>
<td>0.47</td>
<td>0.92</td>
<td>0.23</td>
<td>0.94</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Core 06W</th>
<th>Ti</th>
<th>Al</th>
<th>Cu</th>
<th>Zn</th>
<th>V</th>
<th>Cr</th>
<th>Ni</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1</td>
<td>0.94</td>
<td>0.81</td>
<td>0.40</td>
<td>0.83</td>
<td>0.75</td>
<td>0.71</td>
<td>0.77</td>
</tr>
<tr>
<td>Al</td>
<td>0.94</td>
<td>1</td>
<td>0.88</td>
<td>0.46</td>
<td>0.87</td>
<td>0.77</td>
<td>0.78</td>
<td>0.84</td>
</tr>
<tr>
<td>Cu</td>
<td>0.81</td>
<td>0.88</td>
<td>1</td>
<td>0.25</td>
<td>0.91</td>
<td>0.78</td>
<td>0.83</td>
<td>0.88</td>
</tr>
<tr>
<td>Zn</td>
<td>0.40</td>
<td>0.46</td>
<td>0.25</td>
<td>1</td>
<td>0.23</td>
<td>0.16</td>
<td>0.44</td>
<td>0.41</td>
</tr>
<tr>
<td>V</td>
<td>0.83</td>
<td>0.87</td>
<td>0.91</td>
<td>0.23</td>
<td>1</td>
<td>0.95</td>
<td>0.61</td>
<td>0.95</td>
</tr>
<tr>
<td>Cr</td>
<td>0.75</td>
<td>0.77</td>
<td>0.78</td>
<td>0.16</td>
<td>0.95</td>
<td>1</td>
<td>0.45</td>
<td>0.92</td>
</tr>
<tr>
<td>Pb</td>
<td>0.71</td>
<td>0.78</td>
<td>0.83</td>
<td>0.44</td>
<td>0.61</td>
<td>0.45</td>
<td>1</td>
<td>0.65</td>
</tr>
<tr>
<td>Ni</td>
<td>0.77</td>
<td>0.84</td>
<td>0.88</td>
<td>0.41</td>
<td>0.95</td>
<td>0.92</td>
<td>0.65</td>
<td>1</td>
</tr>
</tbody>
</table>
and more recently by Cloquet et al. (2006). As underlined by these authors, the second trend cannot be explained by the contribution of leaded gasoline. Instead, the new trend follows the European Standard Lead Pollution line ("ESLP"), which was defined by Haack et al. (2003), as "the average lead of the era of industrialization in Europe" (except Pb-gasoline), at least between the Alps and Scandinavia. The ESLP line can contain a mixture of sources that include crustal dust, emissions from lignite, coal, oil and gas power plants, from cement factories and domestic combustion as well as lead derived from geologically young ore deposit (Cloquet et al., 2006). In the Misen bog, this trend is clearly defined by the $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$. Lead isotopic ratios of the recent samples are reported together with radiogenic industrial Pb sources from Europe (Fig. 5b). The recent samples are close to the mean composition of European metallurgical plants confirming the second linear trend. The topmost sample (dated AD 2003) from De Vleeschouwer et al. (2007) also fell within the trend indicated by ESLP. The Pb isotopic ratios of this study show that the Misen bog is influenced by a mixture of local and regional anthropogenic sources. Because the recent Misen samples fit with the EPSL line, we conclude that the Misen site represents a regional record of European pollution, at least for lead.
4.2.2. Cluster analysis

To confirm the source interpretation made with Pb isotopes and to better evaluate the origin and behavior of trace metals in the Misten bog over the last 600 years, we carried out a Hierarchical Cluster Analysis (HCA) on the elemental geochemistry of the core 01W. This statistical approach allows the identification of any linear relationship between different trace metals AR.

For the core 01W, an HCA calculation, was first performed on all on all standardized trace metals AR using STATISTICA software. The obtained dendrograms identify three clusters of trace metals AR (Fig. 6):

- the first group AR includes V, Cr, Co, Ni, Cu, Cr, Al, Ti and Sb
- the second group is defined by AR of Pb and As
- the third group is composed of the potentially mobile elements Zn and Cd.

The similarity cluster represents the degree of association between elements. The higher value on the similarity cluster suggests that the association between these elements is significant and their sources or behavior may be similar. The first and second groups are connected at a higher level (similarity >85%). This relationship suggests common sources or common processes for these elements. The third group contains elements which may undergo post-depositional remobilization (Zn and Cd) as described earlier.

In order to have a chronological control on the statistical information provided by the data, a second HCA calculation on all trace metals AR was performed on successive intervals, i.e., early modern period (n = 6, from AD 1400 to 1700), Industrial Revolution and Leaded Gasoline Era (n = 15, AD 1700–1990) and the Recent period (n = 14, 1990–2008) (Fig. 7a–c). The dendrogram for the early modern period displays three main clusters. Aluminum and Ti distributions are quite similar to some trace metals such as Zn, Pb and Cu. We think that this cluster traces emissions by Pb–Zn ore mining and emissions of large dust particles. This contemporary increase agricultural and mining activity was already suggested by De Vleeschouwer et al. (2007, 2012).

During the Industrial Revolution, the dendrogram points to four groups (Fig. 7b). Groups 1, 2, and 3 are connected at a higher level (similarity >80%), which suggests that the association between these elements is very significant and their sources are similar. The main sources are associated with smelter and refinery production, and coal combustion. The fourth group includes AR of Zn and Cd may reflect a common source or mobility process. Accumulation rates of Al and Ti are similar to the trace metals AR (Fig. 7a–c), which may be explained by the presence of Ti and Al particles in anthropogenic sources. One cluster points out a common and unique source of Co, V, Cr, and Ni.

In addition, we perform a third HCA calculation for trace metals emissions measured in the Walloon region (Brahy, 2010; Fig. 7d) during the phasing out of lead in gasoline (1990–2008) and compare it with trace metals AR derived from the Misten data (Fig. 7c) for the same period (1990–2008). The dendrograms of trace metals AR (except Zn and Cd) and TM emission are quite similar pointing out the validity of the statistical approach to estimate the common sources of immobile trace metals in peat cores.

4.3. History of atmospheric deposition of trace metals in the Misten bog

4.3.1. Early modern period (from AD 1400 to 1700)

Enrichment factors and AR of trace metals increase slightly during this period (Figs. 3, 4). The Pb AR varies between 1 and 3 mg m⁻² yr⁻¹, Cu AR (0.01–0.09 mg m⁻² yr⁻¹), Sb AR (0.01–0.02 mg m⁻² yr⁻¹), Ni AR (0.03–0.11 mg m⁻² yr⁻¹), As AR (0.08–0.18 mg m⁻² yr⁻¹), Cr and V AR (0.1–0.2 mg m⁻² yr⁻¹), Co AR (0.02–0.03 mg m⁻² yr⁻¹), Cd AR (0.1–0.2 mg m⁻² yr⁻¹). Lead and Zn AR show an increase by a factor of 20–100 compared to other trace metal ARs. This increase is represented by a shift in Pb isotope signatures (²⁰⁶Pb/²⁰⁷Pb = 1.177 and ²⁰⁶Pb/²⁰⁹Pb = 2.086) which are in agreement with the field of the Belgian ores. The extraction of these ores during this period is reported in historical documents (Dejonghe, 1998).

4.3.2. Industrial Revolution and unleaded gasoline (from AD 1750 to 1990)

Trace metals concentrations increase in parallel with a small decrease in the ²⁰⁶Pb/²⁰⁷Pb ratio. During this period, the local mining activity (Dejonghe, 1998) along with coal combustion and metal smelting added large quantities of anthropogenic aerosols to the atmosphere. Coal production started in Belgium in 1830 (Rutledge, 2011) and increased significantly to reach its maximum (~30 million metric tons yr⁻¹) between AD 1927 and 1955. Schmitz (1979) and Dejonghe (1998) showed that the Belgian Zn and Pb industry was established around AD 1830 and the Cu industry around 1905 AD.

This strong increase in atmospheric pollution is recorded in the Misten bog by an increase of trace metal ARs by a factor of 8–15 as compared to the period pre-1750. This increase in trace metal ARs is linked to the predominance of coal combustion and metal smelting in Belgium/Europe during this period (AD 1937–1954). After 1953, ²⁰⁶Pb/²⁰⁷Pb ratio drops to lower values (1.147) reflecting the higher importance of gasoline Pb contributions. This observation agrees with the observation of Von Storch et al. (2003), who proposed that Pb gasoline was the dominant anthropogenic source of Pb in 1965. The introduction of leaded gasoline increased from 1930 to a maximum in the 1970's (Von Storch et al., 2003). The progressive reduction of lead in gasoline started in 1972 (Von Storch et al., 2003).

The maximum EFs for V, Cr, Ni, Cu, As, Pb and Co Sb occurred between AD 1937 and 1995 (Fig. 3). Cobalt and Sb were only analyzed in core 01W. These enrichments are due to the important local and/or regional contamination level. Mostly critically, the bog is located at 20 km south of the Pb–Zn ore deposits in eastern Belgium (Dejonghe, 1998) and 300 km from the industrial Ruhr Eifel Area. However, the highest EF values for Zn and Cd are observed during AD 1957–2004, which might be explained by remobilization, like plant uptake.
Between AD 1991 and 1996, all trace metal ARs, in core 01W, continued to increase (Fig. 4) to reach their maxima (Pb AR = 116 mg m\(^{-2}\) yr\(^{-1}\), Cu AR = 8 mg m\(^{-2}\) yr\(^{-1}\), Sb AR = 1.5 mg m\(^{-2}\) yr\(^{-1}\), Ni AR = 1.1 mg m\(^{-2}\) yr\(^{-1}\), As AR = 2.5 mg m\(^{-2}\) yr\(^{-1}\), Cr AR = 8 mg m\(^{-2}\) yr\(^{-1}\), V AR = 6 mg m\(^{-2}\) yr\(^{-1}\), Co AR = 0.5 mg m\(^{-2}\) yr\(^{-1}\), Cd AR = 90 mg m\(^{-2}\) yr\(^{-1}\), and Zn AR = 90 mg m\(^{-2}\) yr\(^{-1}\)). However, in core 06W trace metal ARs reach their maximum between 1930 and 1990 (Fig. 4b). This discrepancy is again explained by the fact that 01W was taken on a hummock while 06W was taken between a hummock and a hollow, provoking difference in particle...
deposition. The increase of trace metals AR in Misten peat samples is marked by a decrease in isotopic ratios $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{206}$Pb. This shift is linked to the predominance of Belgian smelter and refinery production during that period.

Belgian smelter and refinery production (Pb, Cu and Zn) reached a maximum in AD 1978 (Schmitz, 1979), while coal consumption was at its maximum in Europe. From AD 1980 to 1990, coal consumption was about 22 million metric tons in Belgium, 50 million metric tons in France, and 500 million metric tons in Germany (Rutledge, 2011). Consequently, coal consumption, metallurgical activities and industrial development were the predominant source of pollution. Agricultural activities (e.g. pesticides and fertilizers) can also affect the concentrations of trace metals (Nziguheba and Smolders, 2008). Stevens and Van Wesemael (2008) show that the agricultural activities in Belgium increased steadily from 1890 to 1990, and decreased after 1990 to present.

4.3.3. Unleaded gasoline (from AD 1990 to 2008)

In both cores, the trace metal ARs decrease from AD 1987—1995 to AD 2006—2010, in parallel with an increase of the isotopic ratios $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{206}$Pb. The reduction in trace metal ARs from 1987—1995 to 2006—2010 is very similar to the decrease in coal consumption in Europe and the trace metal atmospheric record in Cu, Ni, As, Cr, Cd, Zn, Pb and Sb. This study shows the heterogeneity in peat accumulation and to study the influence of regional European pollution. This study shows that ombrotrophic bog may be an excellent and accurate archive of some trace metals (V, Cr, Co, Ni, Cu, As, Pb and Sb).

Acknowledgments

This study was funded by the Walloon Region and the FNRS. M. Allan received funding through a PhD grant from the government of Syria. We also thank Gunnar Mallon, Mona Court-Picon, Freddy Dambon, Michel Mathijs and Maurice Streefl for their help with the peat sampling, as well as people at the OMP laboratory for ICP-MS analyses and discussion. W. Shoytk (University of Heidelberg) is warmly thanked for loaning his Ti-Wardenaar corer and for having let us use the peat cutting as well as the ultracore microwave facilities at the IES (University of Heidelberg, Germany). We thank Konrad Tudyka and Agnieszka Wszisniowska for their help with the $^{14}$C sample preparation. Pascal Mertes (DNF-Belgian Forest and Nature Ministry) is also acknowledged for providing us with the official authorization for coring the Misten bog. The WD-XRF data acquisition was made possible by Richard Bindler (Uméa University) through a research grant from the Kempe Foundation, which also provided a post-doc fellowship to F. De Vleeschouwer in 2010.

References

Brahy, V., 2010. Anthropogenic impacts in North Poland over the last 1300 years: deposition of pollution. Agricultural activities (e.g. pesticides and fertilizers) can also affect the concentrations of trace metals (Nziguheba and Smolders, 2008). Stevens and Van Wesemael (2008) show that the agricultural activities in Belgium increased steadily from 1890 to 1990, and decreased after 1990 to present.

5. Conclusion

The Misten bog in Eastern Belgium provides a high resolution record of the trace metals and Pb isotope signatures over the last 600 years. The general agreement in trace metals concentration profiles in the cores 01W and 06W suggest that all investigated trace metals, except Zn and Cd, are conserved in the Misten bog. This study shows the utility of taking more than one core to show the heterogeneity in peat accumulation and to study the mobility of trace metals. For all trace metals, the maximum AR is found near the surface of the bog, in peat layers dated AD 1930—1995.

During the Industrial Revolution our cluster analysis and Pb isotopic ratios indicate diverse sources of atmospheric contamination (coal, industrial, steel production, road dust) for all studied trace metals. The upper Misten section is in agreement with measured emissions in the Walloon region.

The history of trace metals in the Misten bog is in agreement with other European records, reflecting the influence of regional European pollution. This study shows that ombrotrophic bog may be an excellent and accurate archive of some trace metals (V, Cr, Co, Ni, Cu, As, Pb and Sb).


Shotyk, W., Krachler, M., Martinez-Cortizas, A., Cheburkin, A.K., Emons, H., 2002. Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the 14C "bomb pulse curve". Geochimica Cosmochimica Acta 67 (21), 3991–4011.


