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Reconstructing historical atmospheric mercury deposition in Western Europe using: Misten peat bog cores, Belgium

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HIGHLIGHTS

- ► Study of Hg concentration in four cores from Belgian peat bog.
- ► Reconstruction of Hg deposition over last 1500 years.
- ► Maximum Hg accumulation rates ranging from 90 to 200 $\mu g\ m^{-2} y^{-1}$ are recorded between 1930 and 1980 AD.
- ► The average Hg accumulation rate before the influence of human activities (e.g. 1300 AD) was $1.8 \pm 1\ \mu g\ m^{-2} y^{-1}$.
- ► The predominant anthropogenic Hg sources were coal burning and smelter Hg emissions.

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ABSTRACT

Four sediment cores were collected in 2008 from the Misten ombrotrophic peat bog in the Northern part of the Hautes Fagnes Plateau in Belgium. Total mercury (Hg) concentrations were analyzed to investigate the intra-site variability in atmospheric Hg deposition over the past 1500 years. Mercury concentrations in the four cores ranged from 16 to 1100 $\mu g\ kg^{-1}$, with the maxima between 840 and 1100 $\mu g\ kg^{-1}$. A chronological framework was established using radiometric ^{210}Pb and ^{14}C dating of two cores (M1 and M4). Pollen horizons from these two cores were correlated with data from two additional cores, providing a consistent dating framework between all the sites. There was good agreement between atmospheric Hg accumulation rates in the four cores over time based on precise age dating and pollen chronosequences. The average Hg accumulation rate before the influence of human activities (from 500 to 1300 AD) was $1.8 \pm 1\ \mu g\ m^{-2} y^{-1}$ (2SD). Maximum Hg accumulation rates ranged from 90 to 200 $\mu g\ m^{-2} y^{-1}$ between 1930 and 1980 AD. During the European–North American Industrial Revolution, the mean Hg accumulation rate exceeded the pre-Industrial values by a factor of 63. Based on comparisons with historical records of anthropogenic activities in Europe and Belgium, the predominant regional anthropogenic sources of Hg during and after the Industrial Revolution were coal burning and smelter Hg emissions. Mercury accumulation rates and chronologies in the Misten cores were consistent with those reported for other European peat records.

1. Introduction

Mercury (Hg) has been used for thousands of years and more recently it has been used in a large number of industrial processes (Pacyna et al., 2006). Mercury is a metal that is toxic to humans and wildlife at low concentrations (Morel et al., 1998; Mergler et al., 2007). Natural Hg sources include volcanic activity, erosion and marine emissions (Schroeder and Munthe, 1998). The principal anthropogenic Hg emission sources are coal fired power plants, chlorine production, non-ferrous metallurgy, cement production, and primary and secondary lead and zinc production (Wilson et al., 2006; Pacyna et al., 2006; Pirrone and Mason, 2009). More than 95% of natural and anthropogenic Hg emissions are mainly in elementary form (Hg^0) with a residence time of 6–12 months in the atmosphere (Schroeder and Munthe, 1998; Fitzgerald and Lamborg, 2007; Pirrone and Mason, 2009). Long-range transport of Hg emissions has resulted in the contamination of remote ecosystems, generating a serious environmental problem that transcends national boundaries (Pirrone and Keating, 2010). Hylander and Meili (2003)

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suggested that the current rate of global Hg emission (until 2000) to the atmosphere was approximately 3 times higher than during the pre-Industrial Revolution. The Industrial Revolution was a period from 1750 to 1850 marked by an increase in industrial activities, coal burning, and petroleum use. Similarly, Lindberg et al. (2007) estimated that atmospheric Hg deposition to remote ecosystems globally had increased by a factor of 3 since the start of the Industrial Revolution (1700 AD). To determine the regional versus global contributions, it is important to quantify the origin of this atmospheric Hg and its spatio-temporal variations.

Several types of environmental archives (lake and marine sediments, ice and peat) have been used to provide information about Hg deposition during the last thousand years (e.g., Gobeil et al., 1999; Bindler et al., 2001; Biester et al., 2002; Roos-Barraclough et al., 2002; Givelet et al., 2004a, 2004b). Peat records from ombrotrophic peatlands that receive inputs by way of the atmosphere are unique archives of anthropogenic and natural deposition of trace elements (e.g., Shotyk et al., 1996, 2001; Martinez Cortizas et al., 1997, Farmer et al., 2009; Zaccone et al., 2009; Manneville et al., 2006).

Data from ombrotrophic peat bogs, (Martinez Cortizas et al., 1999; Roos-Barraclough et al., 2002; Biester et al., 2002; Shotyk et al., 2003) have been utilized to reconstruct the evolution of atmospheric Hg deposition over long-term periods (e.g. the Holocene). In these studies, the Hg accumulation rate was calculated by combining the accumulation rate and density of the peat bog and Hg concentration (Madson, 1981; Jensen and Jensen, 1990; Norton et al., 1997; Martinez Cortizas et al., 1999; Roos-Barraclough et al., 2002; Givelet et al., 2004a, 2004b), and Hg was assumed to be immobile and well preserved in ombrotrophic peat (e.g. Benoit et al., 1998; Roos-Barraclough et al., 2002; Givelet et al., 2004a, 2004b; Shotyk et al., 2003, 2005). However, most authors (e.g. Rydberg et al., 2010; Biester et al., 2003) have suggested that Hg concentrations in peat bogs could be affected by natural biogeochemical processes such as peat decomposition and early diagenesis. This hypothesis was tested, but not validated, by Outridge et al. (2011) using an age-dated permafrost peat core from Northern Canada. Thus to use Hg concentrations in peat bogs as a record over time requires a precise chronological control of peat accumulation, especially in the acrotelm zone or the layer generally above the water table that can be both aerobic and anaerobic (Quinty and Rochefort, 2003). In this layer, unlike the catotelm or bottom layer that is below the water table, Hg should not be bound to recalcitrant and stable humic acids (Zaccone et al., 2009). Rydberg et al. (2010) further suggest that the local variability in Hg accumulation rates for different cores from the same bog may be explained by the variation in vegetation type in Swedish mire. In several studies a multi-core approach was used to reconstruct historical Hg accumulation in bogs (Benoit et al., 1998; Bindler et al., 1999, 2004; Klaminder et al., 2003; Novák et al., 2003; Coggins et al., 2006; Cloy et al., 2008; Martinez Cortizas et al., 2012; Zuna et al., 2012). By using 14 ombrotrophic peat cores collected from NW Spain, Martinez Cortizas et al. (2012) showed that the multi-core sampling provides good opportunities to evaluate the vertical, spatial and temporal records of atmospheric Hg deposition. To identify the different factors that influence mercury accumulation within and between sites we collected four cores in the Belgian Misten peat bog. The Misten peat has the two distinct layers (acrotelm/catotelm) controlled by the hydrological conditions. The microbial activity in the acrotelm is more rapid than in the catotelm. By coupling element chemistry with ^{14}C, ^{210}Pb dating, and pollen history, our aims were to: (1) quantify the net atmospheric Hg accumulation rates in the region of Misten (Belgium) over the last 1500 years; (2) determine the intra-site variability in Hg accumulation rate; (3) evaluate down core Hg mobility, and (4) compare the Misten record with Hg records from other European sites.

2. Materials and methods

2.1. Sampling site and sample collection

The Misten peat bog is located in Eastern Belgium, ~5 km from the German border (Fig. 1). The peat bog surface has higher relief than surrounding area. A titanium Wardenaar corer from the University of Heidelberg was used to recover the upper first meter. The length of all peat cores was between 90 and 110 cm. A Belarus corer was therefore used to core deeper (core name MIS-08-01b). Maximum peat thickness reaches up to 8 m (Wastiaux and Schumacker, 2003), dating back to 9000 years (De Vleeschouwer et al., 2007). Based on geochemical parameters (Ca/Mg ratio, Sr concentrations), the Misten peat bog described as ombrotrophic for the upper 6.5 m and minerotrophic between 6.5 and 8 m. Although, ombrotrophic peatlands receive inputs from the atmosphere, the minerotrophic component also receives water influenced by surrounding soils and rocks.

The four peat cores MIS-08-01W (M1), MIS-08-04W (M2), MIS-08-05W (M3) and MIS-08-06W (M4) were collected in February 2008 using a Wardenaar corer (Fig. 1) in the most protected part of the natural reserve "Les Hautes-Fagnes". The distance between the four cores was 50 to 100 m. The length of all peat cores was between 90 and 110 cm. Following the protocol described by Givelet et al. (2004a, 2004b), the cores were frozen (−40 °C) and cut by a stainless steel band saw (thickness of each sample ~1.5 cm). The peat samples were freeze-dried (at −40 °C, pressure ~ 10^{-1} mbar) during approximately 1 week and powdered using an agate ball mill.

2.2. Ash content and humification

The mineral matter content of the peat, defined as "ash content", was determined for all samples in cores M1 and M4 and every other sample in cores M2 and M3. Peat samples were dried at 105 °C over night and subsequently weighed to obtain the dry weight. Between 0.1 and 1 g of dried peat was then placed in oven at 550 °C for 6 h, to remove all organic matter by combustion (Chambers et al., 2011).

The degree of humification was estimated by colorimetry on peat alkaline extracts (Chambers et al., 2011). Two hundred milligrams of dried peat were reduced to powder and placed in an Erlenmeyer flask. One hundred milliliters of NaOH (8%) were added and the solution was boiled for 1 h. After cooling, the solution was diluted to 200 ml with MQ distilled water, then homogenized and filtered using no.1 Whatman filter paper. Fifty milliliters were taken and diluted with an equal volume of distilled water, and then directly placed in a spectrophotometer at the Scientific Station of the "Hautes Fagnes" (SSHF, University of Liege), for absorbance measurement at 540 nm. For every 10 samples, a standard with a humification level of 100% (Humic acid technical, ALDRICH) was included in the measurement. The ratio between the absorption values in the peat samples and peat standard was transformed to humification percentage.

2.3. Hg analysis

Mercury concentration was measured using a Milestone® DMA-80 at the Geosciences Environment Toulouse laboratory (France). All samples of the upper 25 cm of the cores and every other sample below this depth were measured. From 20 to 120 mg of dried bulk peat samples were used for analysis. Mercury concentrations were measured using an atomic absorption spectrophotometer after combustion and reduction of all forms of Hg to elemental Hg. Calibration was performed using ombrotrophic peat reference material (NIMT/UOE/FM/001/NIST 1575) and peach leaves (NIST 1547). During each series of analyses, standards were analyzed three times before the first sample then between the samples. The average measured values were $162 \pm 9 \mu g\ kg^{-1}$ (n = 9) for NIMT