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Distribution of lead and mercury in Ontario peatlands☆

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ABSTRACT

While considerable attention has been given to the measurement of mercury (Hg) and lead (Pb) concentrations and accumulation in detailed peat cores in central Canada, the geographic distribution and density of sampling are generally limited. Here, we use the Ontario Peatland Inventory to examine broad patterns of Hg and Pb concentration with depth, based on 338 peat cores (containing >1500 analyzed samples) from 127 bogs, fens and swamps located in southeastern, northeastern and northwestern sections of Ontario. Overall, Hg concentrations averaged 0.05 μg g^{-1} and that of Pb averaged 10.8 μg g^{-1}. Maximum values in the top 50 cm of the profiles are 0.08 μg g^{-1} and 26.2 μg g^{-1} for Hg and Pb, respectively. The ratio between these values (surface) and the values from below 100 cm (background), where peat likely accumulated before 1850 and industrial activities were limited, are 2.3 and 6.6 for Hg and Pb, respectively. The highest surface:background concentration ratios are generally found in the westernmost part of the province and in the southeast for Hg and around areas that are more heavily populated for Pb. Our results show that a vast amount of Hg and Pb are stored in Ontarian peatlands, although the spatial distribution of these stores varies. The rapid decomposition of peat in a changing climate could release these pollutants to the atmosphere.

1. Introduction

Peatlands are ecosystems that are characterized by a temporally incremental accumulation of organic matter (peat) because of the imbalance between organic matter production and decomposition. Because of this accumulation of organic matter and its ability to retain elements, peatlands store large amounts of atmospheric pollutants and have been used as historical archives to estimate changes in the atmospheric loading of lead (Pb) (e.g. Outridge et al., 2011; Weiss et al., 2002; Zaccone et al., 2007) and mercury (Hg) (e.g. Allan et al., 2013; Ukonmaanaho et al., 2004; Zaccone et al., 2009).

Bogs are often reported as the best type of peatland to record long-range and local changes in atmospheric deposition of airborne pollutants because they only receive atmospheric water inputs and are not influenced by groundwater, at least in the upper part of peat (Benoit et al., 1998; Shotyk, 1996). They are also known to retain metals such as Hg and Pb as they bind well with organic acids in the peat (Shotyk and Le Roux, 2005). While fens and swamps are not typically used as atmospheric deposition records, they are important components of the boreal landscape and could be significant sinks of Pb and Hg and potential sources of contaminants to downstream ecosystems (Kolka et al., 1999a; Rothwell et al., 2008; St. Louis et al., 1996).

Variations in natural, background sources in the elements can be important as dust deposition has varied throughout the Holocene. However, many studies have clearly shown an increase in Hg and Pb peat concentration concomitant with an increase in human activities, with the earliest impacts detected thousands of years ago in Europe and a great acceleration of deposition concurrent with the industrial revolution (e.g. De Vleeschouwer et al., 2010). In North America, this increase can be observed starting in the 15th century corresponding to biomass burning by native North Americans and is continued with the biomass burning by settlers through the 19th century and peaks in the 1950s (Givelet et al., 2003; Riley, 2013). The main anthropogenic sources of Hg since the beginning of the industrialized period are silver, gold and mercury production, fossil fuel combustion (mainly coal), and

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waste incineration (Pacyna et al., 2006; Streets et al., 2011). For Pb, the main anthropogenic source was car fuel combustion until the ban of Pb addition to petrol in the United States, Canada and Europe in the 1980s, and emissions from industrial processes (Bollhöfer and Rosman, 2001).

High resolution measurements of the concentration and accumulation of Hg, Pb and other trace elements have been made for a few detailed peat cores in central Canada, allowing precise assessment of the timing of increased heavy metal deposition (Givelet et al., 2003; Pratte et al., 2013; Shotyk et al., 1990; Shotyk and Krachler, 2010). However, the geographic representativeness of these cores is limited. Here we use the Ontario Peatland Inventory to examine broad patterns of Hg and Pb concentrations with depth in bogs, fens and swamps within a 450 000 km^2 area in Ontario. Because Hg and Pb both cause serious environmental and health concerns (Tchounwou et al., 2012), a better understanding of their distribution in the landscape and the overall amount that is stored in peatlands as a 'legacy' of past pollution (e.g. Amos et al., 2013) is critical in a context where peatlands may experience enhanced degradation in response to climate change (Frolking et al., 2011). Our objectives are to (1) provide baseline estimates of Hg and Pb concentrations and total inventories in Ontario peatlands; (2) assess broad temporal changes in Hg and Pb accumulation; and (3) explore spatial patterns in surface peat Hg and Pb concentration in Ontario.

2. Materials and methods

2.1. Study area

Sampling sites were part of a large scale survey of peat resources conducted in Ontario and extend from 74°W to 94°W and 43°N to 51°N (Riley, 1989a, 1994a, 1994b). The sites were selected to represent a range of typical peat accumulation conditions. They had to have uniform vegetation cover, be > 100 ha in size and have at least 40 cm of peat accumulation. They were classified into bogs, fens and swamps, depending on their pH, surface peat botanical composition and tree cover (Riley and Michaud, 1994). Bogs had a pH lower than 5.2 and surface peat was dominated by *Sphagnum* remains, whereas fens and swamps have a higher pH and a graminoid, woody or brown-moss dominated surface peat. Swamps have a tree or tall shrub cover higher than 25%.

The survey generated the analysis of 1579 samples for Hg concentration and 1510 samples for Pb concentration, from 338 peat profiles sampled in 127 different peatlands (some peatlands were a mosaic containing different peatland types). In total, 154 profiles were from bogs, 96 were from fens and 88 were from swamps.

2.2. Data collection

Peat cores were sampled using a Mini-Macaulay or Hiller sampler and divided into four intervals or more for deeper profiles, based on their botanical composition and apparent degree of humification. The highest and lowest depth of each section was recorded, as well as the degree of humification based on the von Post index, ash content, botanical content of the peat, and the chemical composition of the samples (Riley and Michaud, 1994). The stoichiometry of carbon and macro-nutrients was analyzed by Wang et al. (2015).

For details on the Pb and Hg elemental analyses, see Riley (1989b). Briefly, Pb was determined by treating the samples with HNO_3, HF and H_2SO_4, HCl and H_2O_2, or, alternatively, by dry-ashing the samples and treating them with boric acid and lithium carbonate and dissolving them with H_2O:HNO_3. Elemental concentration was determined using inductivity coupled argon plasma emission spectrometry, with automatic background correction. For Hg, after treatment of the dried peat samples with HNO_3 and H_2SO_4, $KMnO_4$ was added, and elemental concentration was determined by cold vapor generation and flameless atomic absorption. The analytical techniques date from the 1980s and the detailed report (Riley, 1989b) suggests that they tended to underestimate concentrations of peat Hg and Pb compared to standard materials.

2.3. Data treatment

To generate the average elements profile with depth, we used the average depth of each sample, and binned them by 10 cm depth intervals for the top 250 cm of the profile, and by 20 cm depth intervals for the rest of the profile. As the profiles are not dated, we used average vertical peat accretion rates derived from the literature for similar peatlands (Turunen et al., 2004) to determine the portions of the profiles where humans had the most influence on Hg and Pb deposition. Considering that industrialization of southeastern Ontario started around 1850, we set that date as the cutoff. Using an average accretion rate of 3.5 mm $year^{-1}$ for 138 years (as the cores were sampled in 1984), we get a depth of 48.3 cm for 1850, rounded to 50 cm. In other terms, we identified the top 50 cm as the zone of the profile where we were likely to find traces of higher Hg and Pb deposition of industrial origin.

The most accurate method to calculate the proportion of a metal found in peat that is from an anthropogenic source is to calculate chemical ratios between the pollutant and elements principally derived from mineral weathering such as titanium (Ti), and compare these values with the ratios for the upper continental crust (Shotyk et al., 2000). The concentration of Ti was not available for our samples, so we used a different approach. Ratios between the recent Hg and Pb concentration and what we considered as background values were calculated. We examined each profile individually and selected the highest Hg or Pb concentration value available in the top 50 cm of the profile and divided it by the weighted average of the values found below 100 cm, so likely older than 1000 yrs AD (assuming that peat grows upwards at ~1 mm per year on average for the top 100 cm of the profile, Rydin and Jeglum, 2013). At that depth, human influence on Hg and Pb concentrations are likely small in Ontario.

To calculate approximate average Hg and Pb accumulation recent rates, we applied the C:Hg and C:Pb ratios of the top 50 cm of the profiles (C values in Wang et al., 2015) to the average acrotelm peat C accumulation rate of 73 g C m^{-2} yr^{-1} (Turunen et al., 2004). It should be noted that this average C accumulation rate was calculated based on bog profiles only. For Hg and Pb accumulated lower in the profile, we used ratios from the part of the profiles below 50 cm and the average long-term peat accumulation rates of 23 g C m^{-2} yr^{-1} (Loisel et al., 2014).

Inventories of Hg and Pb were calculated based on average peatland depth and average bulk densities for each peatland type (Riley, 1989a, 1994a, 1994b). Using these average Hg and Pb inventories and bog, fen and swamp areas of 246 750 km^2, 124 980 km^2 and 2020 km^2, respectively (Tarnocai et al., 2011), we calculated total Hg and Pb inventories for Ontario peatlands.

The significance of a Hg and Pb relationship with other chemical elements (Fe and Mn) was tested using an analysis of variance on the slope of the regressions. Normality of the data was tested using a Shapiro-Wilk test. All tests use a significance level (α) of 0.05.

3. Results

3.1. General patterns

The average Hg and Pb concentrations of all samples are 0.05