Reconstructing the history of atmospheric metal deposition
from analyses of ombrotrophic peatlands along the St. Lawrence Valley

M.Sc. proposal
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**Introduction**

Industrialisation created numerous environmental problems such as atmospheric pollution by trace metals, their dispersion and accumulation in soils and transfer into the food chain. Some of these elements (e.g., Pb, Cd, Hg) are among the most toxic to human and animal. For example, the addition of tetraethyllead to gasoline, coupled to the metal’s relatively long residence time in the atmosphere (~ 5-10 days) caused long-range dispersion and serious health effects (Sturges and Barrie, 1987). Cadmium, released to the atmosphere from the roasting of ore, has also a relatively long residence time in the atmosphere (~ 1 week) and can be transported over long distances (Morel and Malcolm, 2005). Mercury has an atmospheric residence time of about 1 year, is dispersed homogeneously through intra-hemispherical mixing, and its bioaccumulation has been documented far from point sources (e.g., ore roasting, burning of industrial and municipal waste) (O’Driscoll et al., 2005). A precise reconstruction of the rates of heavy metal atmospheric deposition is difficult due to their remobilization or transformation in sedimentary environments (marine, coastal and lake sediments).

Due to their anoxic conditions, peatlands are characterized by net organic accumulation over decomposition (Clymo, 1987). Ombrotrophic peatlands get their nutrients from the rainfall, which is a very poor source of minerals. These systems are recognized as good archives of trace metal accumulation, mainly Pb (Bindler, 2006; Shotyk and Krachler, 2010) but also Hg (Bindler, 2006), Cu, Ni and Zn (De Vleeschouwer et al., 2007). In the recent years, a growing number of studies have been published in which peat bog cores have been used as archives of trace metal deposition in Europe (see Bindler, 2006 and Shotyk et al., 2003 for a list). In contrast, very few similar studies have been carried out in North America (Shotyk and Krachler, 2010).

When lead is emitted to the atmosphere, it keeps the isotopic composition of its source. Hence, it is possible to use its isotopic signature to discriminate between natural and anthropogenic sources (Sturges and Barrie, 1987). Until 1984, the lead added to gasolines in Canada and the U.S.A. came from different ore deposits. In Canada, the lead in gasoline was coming mainly from the Barthurst deposit in New Brunswick (Pb-206/207 = 1.16) while it originated from Mississippi Valley ores (Pb-206/207 = 1.30) in the U.S.A (Sturges and Barrie, 1987). Since the mid-80’s, this distinction became blurred as a greater variety of ores and recycled Pb were used in different industrial processes (Sturges and Barrie, 1987).

In this study, peat cores collected in four different peatlands along the St. Lawrence Valley will be analysed to fulfill the following objectives:

- Reconstruct the history of atmospheric Pb, Cd, As, Hg, Ni and Zn deposition along the St. Lawrence Valley by using peat cores from ombrotrophic bogs.
- Determine the isotopic composition of lead in the peat sequences to distinguish between natural and anthropogenic sources.
• Measure the concentration of other elements (Sc and/or Ti, Fe, Mn, C/N) to assess the post-deposition behaviour of the trace elements.
• Correlate the results with diagenetic reconstructions of trace metal deposition from lake sediment studies

The historical reconstructions of trace metal deposition can be used to evaluate the effectiveness of environmental policies and to determine pre-industrial background concentrations (Shotyk and LeRoux, 2005). Scandium and titanium concentrations will be measured to evaluate mineral contributions to deposition. Strontium will be used in combination with vegetation type to assess the ombrotrophy of the peat sequences. Iron and manganese are used to track oscillations of the redox boundary near the water table. Carbon and nitrogen will be measured to assess the level of peat decomposition. All these post-depositional phenomena can potentially remobilise trace metals accumulated in peat. Hence, it is important to measure the concentrations of these elements as well as those of the trace metals of interest.

**Material and methods**

**Sampling and subsampling**

For the purpose of this research three cores were sampled in peatlands distributed along the St. Lawrence Valley. The Mirabel and Frontenac Bogs were sampled using PVC pipes and the Baie Bog, near Baie-Comeau, was sampled using a 8x8x50 cm stainless steel box corer. A fourth core is to be collected at Mer Bleue Bog near Ottawa.

Cores subsampling was carried out in the lab at 1-cm intervals using plastic equipment and a ceramic knife to avoid metal contamination. All the equipment was acid washed beforehand in a 10% HCl solution and rinsed with Milli-Q water between each subsampling. The outer half a centimeter from each slice was trimmed and discarded as those could have been contaminated by smearing during sampling or core extrusion (Givel et al., 2004). Half the samples were kept fresh in plastic re-sealable bags (Ziploc) and the other half were freeze-dried and ground in a mortar with pestle for geochemical analysis.

**Trace metals analysis**

About 200 mg of each peat subsample will be digested in 4ml of 30% ultrapure H$_2$O$_2$ and 3ml of ultrapure 70% HNO$_3$ and then heated at 60°C for 12 hours (modified from Shotyk et al., 1998). The digestates will then be diluted to an acid concentration of around 0.5%. Analytical, acid and Milli-Q water blanks will be measured to identify possible sources of contamination. Peach leaves NRC standards will also be analysed to determine the accuracy of our analytical protocols.

$^{210}$Pb Dating of the Cores
$^{210}$Pb dating is being carried out on every other sub-sample (i.e., every at 2-cm intervals) from the surface to a depth of 30 cm. Aliquots of 0.1-0.4 g of peat samples were spiked with $^{209}$Po tracer and digested in Teflon vials using aqua regia. After the aqua regia attacks, a few drops of concentrated 30 % H2O2 were added and the solution was evaporated to dryness. The residues were then transformed into chloride salts by repeated evaporation with 12 ml of HCl 6M, then dissolved in 0.5 ml of HCl 6M, and 0.2 g of ascorbic acid were added to the solution. Po isotopes were deposited on an Ag disc (Hamilton and Smith, 1986) and the activity was measured by alpha spectrometry. The constant rate of supply will be used to obtain the dates.

$^{137}$Cs Dating of the Cores

Peaks of 137Cs are normally recorded in the sediments ca. 1963 AD due to nuclear weapon testing. 137Cs activity will be measured in a selection of samples around 1963 AD previously identified by $^{210}$Pb dating. Measurements will be done using 0.4 g of dry peat samples previously ground in homogenous powder using a mortar and a pestle. 137Cs will be determined via its gamma emission at 662 keV. The detector will be calibrated using a standard radionuclide (CLV-1).

$^{14}$C Dating of the Cores

One to two samples of macroremains (Sphagnum, charcoal) per core will be collected for radiocarbon dating. These samples will be sent to a commercial laboratory (University of California, Irvine, U.S.A.).

Lead isotope measurements

Lead isotopes will be measured to identify its sources. Before being analysed, Pb will be purified following standard anionic exchange resin protocol (Poirier, 2006). The isotopic composition will be measured by ICP-MS, the mass bias will be corrected using the thallium doping technique and normalizing the Tl isotopic value by repeated analysis of the NBS-981 standard (Poirier, 2006).

Timelines

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References


