History of atmospheric trace metal deposition along the St. Lawrence Valley (Quebec) using peat bog records

by

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Contribution of the authors

This thesis is the result of my M. Sc. research project in the Department of Earth and Planetary Sciences at McGill University. This thesis consists of three chapters. The first chapter is a general introduction and a review of atmospheric trace metal and peatlands studies. The rationale of the project is included at the end of the general introduction. The second chapter is a paper destined for publication. It contains a description of the experimental work carried out and how the established objectives were achieved. This chapter also includes the results of the study and their interpretation. The final chapter is a general conclusion with recommendations for future work. The subject of this thesis was proposed by Professor Alfonso Mucci. Core collection was completed by myself and Professor Michelle Garneau under the guidance of Professors Mucci and Garneau. All laboratory and analytical work was completed by myself. Professors Alfonso Mucci and Michelle Garneau provided guidance on the methodology and advised me with the processing and interpretation of the data and contributed to the preparation of this thesis.

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Abstract

Human activities, especially since the Industrial Revolution, have left a legacy of trace metal contamination that is potentially harmful for natural ecosystems and human health (e.g. As, Cd, Pb) and affected their geochemical cycles. Atmospheric metal pollution is recorded in different environmental archives such as lake and marine sediments, snow and ice and peat bogs. Among these archives, peat bogs have proven to be effective in reconstructing the history of atmospheric metal deposition throughout Europe, but few studies have been carried out in North America or in Quebec. Being an important natural wind corridor, oriented from south-west to north-east, the St. Lawrence Valley is affected by long-range transport of contaminants. The present study focuses on the reconstruction of the history of atmospheric As, Cd, Ni, Pb and Zn deposition in surface cores (<100 cm) from three peat bogs along the St. Lawrence Valley. Core chronologies were established using ^{210}Pb for the upper horizons and ^{14}C dating for the deeper sections. Metal accumulation rates were computed from measured concentrations and core chronologies. Stable lead isotopes (204, 206, 207 and 208) were also analysed to distinguish natural and anthropogenic sources of Pb. Results show that the three cores recorded the onset of industrial activities around 1810-1850AD. As, Cd, Pb and, to a certain extent Ni deposition increased to reach a maxima in the 1940s and mid-1960s to early 1970s. Trace metals likely originated from coal-burning and ore smelting during the 19th and the first half of the 20th centuries. Thereafter, the dominant source of Pb became leaded gasolines additives until their phasing-out in the 1970s. Trace metal contents were greater in the two cores recovered in the southwestern part of the St. Lawrence Valley than in the one located 600 km to the northeast. This can likely be explained by their proximity to urban and industrial centers of St. Lawrence and Ottawa Valleys and U.S. Mid-West. The Pb isotope signatures suggest a long-range transport of contaminants from a common regional source (U.S. Mid-West, Great Lakes Region). A rapid decrease in metal accumulation rates since the 1970s suggest that the implementation of mitigation policies was effective in reducing

atmospheric emissions of trace metal. Nevertheless, metal accumulation rates and stable Pb isotopes have not yet returned to pre-industrial values.

Résumé

Les activités humaines, particulièrement depuis la Révolution Industrielle, ont perturbé le cycle géochimique de plusieurs métaux traces potentiellement toxiques (e.g. As, Cd, Pb) avec d'importantes répercussions pour les écosystèmes et la santé humaine. Plusieurs archives environnementales, tels les sédiments marins et lacustres, les tourbières, et les glaciers servent d'enregistrements historiques de la pollution atmosphérique. Parmi celles-ci, les tourbières sont reconnues comme étant des archives fiables pour la reconstruction des dépôts atmosphériques de métaux. Les tourbières ombrotrophes sont fréquemment utilisées en Europe pour reconstruire l'histoire des dépôts atmosphériques de polluants. Ce type d'étude est plus rare en Amérique du Nord, particulièrement au Québec. La vallée du St-Laurent est un corridor naturel important, dominé par des vents du sud-ouest vers le nord-est, et affecté par le transport de contaminants sur de longues distances. La présente étude a pour but la reconstruction historique des dépôts atmosphériques de As, Cd, Ni, Pb et Zn à partir de carottes de surface (< 100 cm) récoltées dans trois tourbières ombrotrophes le long de la vallée du St-Laurent. La chronologie des carottes fût établie à l'aide de datations au ^{210}Pb et ^{14}C. À partir de ces chronologies, les taux d'accumulation de métaux traces d'origine atmosphérique furent calculés. Les isotopes stables du Pb furent aussi analysés afin de distinguer les sources naturelles et anthropiques du Pb. Les résultats démontrent que les trois carottes ont enregistré le début des activités industrielles entre 1810-1850AD. L'accumulation de As, Cd, Pb et, dans une certaine mesure, Ni a augmenté de façon constante pour atteindre des maxima dans les années 1940 et à la fin des années 1960 et début 1970. Les contaminants provenaient probablement de la combustion de charbon et des usines métallurgiques du 19$^{\text{ième}}$ et début du 20$^{\text{ième}}$ siècle. Par la suite, la source principale du plomb fut celle des essences plombées (tétraéthyl-plomb) jusqu'à leur élimination graduelle dans les années 1970. Les taux d'accumulation de métaux sont plus importants dans les deux carottes récoltées dans le sud-ouest de la vallée comparativement à celle située à 600 km au nord-ouest. Ce phénomène peut être expliqué par la plus grande proximité des centres urbains et industriels du Mid-Ouest des États-Unis et des Grands Lacs

ainsi que des vallées du St-Laurent et d'Ottawa des deux sites du sud-ouest par rapport à celui au nord-est. Les isotopes du plomb suggèrent que les contaminants furent transportés sur de longues distances et tiennent leur origine de sources régionales, telles que le Mid-Ouest des États-Unis ou la région des Grands Lacs. Une diminution rapide des taux d'accumulation de métaux à partir des années 1970 suggère que les mesures de mitigation des émissions atmosphériques mises en place durant cette période furent efficaces. Par contre, les taux d'accumulation et la signature isotopique du Pb montrent que des sources anthropiques de métaux persistent puisqu'ils demeurent différents des valeurs préindustrielles.

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Chapter 1: Introduction and Literature review

1.1 Introduction

Since the Industrial Revolution, human activities have affected the global geochemical cycles of potentially toxic elements, with important repercussions on the ecosystems and adverse effects on human health (e.g. As, Cd, Pb). For example, the addition of tetraethylead to gasoline, coupled to the metal's relatively long residence time in the atmosphere (~ 5-10 days) resulted in long-range dispersion of this metal through the atmosphere (Sturges and Barrie, 1987). Exposure to lead is well known to cause neurotoxic effects likely leading to learning deficiencies in children (Nigg *et al.*, 2008; Chandramouli *et al.*, 2009). Furthermore, studies show that arsenic inhalation and ingestion is linked to high cancer rates (Centeno *et al.*, 2002; Chen and Ashan, 2004). Hence, it is important to assess past and actual levels of heavy metals released in the environment.

Atmospheric metal pollution is recorded in different environmental archives such as lake and marine sediments, soils, snow and ice, lichens, and peat bogs. These archives have proven to be effective in reconstructing the history of atmospheric metal contamination. Although subject to local and regional variations, these records show an important increase in Pb emissions starting with the Industrial Revolution (ca. 1800) and reaching a maximum at ca. 1970 AD. These records can also be used to evaluate if different mitigation measures, like the phasing-out of leaded gasoline or the implementation of the Clean Air Act in the U.S.A., are recorded and how effective they have been. For example, Cd, Pb and Zn concentrations in Greenland snow have decreased since Pb was banned as a fuel additive and other industrial emissions in the Northern Hemisphere were curtailed in the 1970s (Boutron *et al.*, 1991). Furthermore, these archives can be used to track trace metal emissions in regions and/or periods where direct historical or archeological data are not available (Le Roux, 2004).

Ombrotrophic peatlands (peat bogs) are peat-accumulating wetlands fed exclusively by nutrients delivered from the atmosphere. Peatlands originate from net accumulation of organic material that records past ecological, climatological or geochemical conditions over time. Peatlands are characterized by a high organic content (usually > 90% dry wt.) for which many trace metals have a strong affinity (Rydin and Jeglum, 2006). Therefore, they are ideal archives of atmospheric metal deposition. In contrast to the extensive amount of work carried out in Europe on the historical reconstruction of atmospheric metal deposition using peat bogs (Shotyk, 1998; Bränvall *et al.*, 2001; Bindler *et al.*, 2008), few similar studies have been conducted in North America and most of the latter focused either on Hg (Benoit *et al.*, 1998; Givelet *et al.*, 2003; Roos-Barraclough *et al.*, 2006) or Pb (Norton *et al.*, 1997; Weiss *et al.*, 2002a; Kylander *et al.*, 2009; Shotyk and Krachler, 2010). Given the large scale emissions of various metals to the atmosphere throughout North America in the last two centuries (Pacyna and Pacyna, 2001), it is important to achieve a more comprehensive and multi-element coverage of this continent (Steinnes and Friedland, 2006).

A number of studies, using archives other than peat bogs, were undertaken in eastern North America, mainly to reconstruct the history of atmospheric Pb and Hg deposition (Ouellet and Jones, 1983; Gobeil *et al.*, 1995; Lucotte *et al.*, 1995; Gallon *et al.*, 2005, 2006) whereas a few studies included other metals such as As, Cd and Zn (Kada and Heit, 1992; Gélinas *et al.*, 2000; Alfaro-De la Torre and Tessier, 2002; Couture *et al.*, 2008).

The St. Lawrence Valley is a natural wind corridor, oriented from the south-west to the north-east, where air masses flow from the centre of the continent to the Atlantic Ocean. A decreasing gradient of atmospheric deposition away from major metal-emitting sources (e.g., coal-fired power plants and smelters) in North Eastern America, particularly the United States' NE, is well documented (Ouellet and Jones, 1983; Carignan and Gariépy, 1995; Simonetti *et al.*, 2000; Evans *et al.*, 2005; Lucotte *et al.*, 2005). For these reasons, the St. Lawrence Valley is well suited for studies of long-range trace metal atmospheric transport.

1.2 Focus of the study

This study focuses on the historical reconstruction of the atmospheric deposition of a number of trace metals (As, Cd, Ni, Pb and Zn) along the St. Lawrence Valley, as recorded in ombrotrophic peatlands distributed from Ottawa (southeastern Ontario) to Baie Comeau (northeastern Quebec). Trace metal concentrations, accumulation rates and enrichment factors are used in this regard. Stable Pb isotopes (204, 206, 207 and 208) are used to identify the origin of Pb pollution (U.S. vs Canadian) as well as to distinguish between natural and anthropogenic sources.

1.3 Literature review

1.3.1 Trace metals

1.3.1.1 Trace metals in the atmosphere

Pb, Zn, Cd, As and Ni are among the most toxic elements to living organisms, all are considered as priority pollutants in accordance with USEPA "Red list". Of these five elements, zinc is the only well documented essential micronutrient for plants and various living organism, including humans. These elements are released to the atmosphere mostly as particulates, either in their elemental state (Pb^0), as complexes (e.g. $PbSO_4$, ZnS, CdS) or adsorbed to other particles (Batonneau *et al.*, 2004). Atmospheric trace metal concentrations in remote areas of the world (such as North Atlantic, Antarctica and Northwestern Territories, Canada) are at least two orders of magnitude lower than in urban environments (Table 1.1), demonstrating that human activities greatly affect trace metal cycles.

The residence time of these elements in the atmosphere depends on their physic-chemical properties, particle size, meteorological conditions and typically averages seven days for As, Cd, Ni and Pb (Rahn, 1976; US EPA, 1982; CEPA, 1994). Using a physical model, Telmer *et al.* (2004) found that within 15 km of a smelter, trace metal deposition is mainly controlled by dry deposition, whereas, beyond 15 km, wet deposition is the dominant process. Metals removed from the atmosphere by wet deposition have a residence time similar to that of water vapor, seven days, and can therefore be transported over long distances (100s-1000s km), depending on meteorological conditions (Telmer *et al.*, 2004). Elements emitted from anthropogenic sources are typically associated to smaller particles (less than 1 μm) while those from natural sources are generally associated with larger particles (greater than 10 μm). Therefore, anthropogenic particles are usually transported over longer distances (Schroeder *et al.*, 1987).

1.3.1.2 Sources of atmospheric trace metals

Anthropogenic sources of trace metals (Pb, As, Cd, Ni and Zn) to the atmosphere include metal processing (mainly smelting), waste incineration, cement production and fossil fuel combustion (Table 1.2). Until the mid-90's, leaded gasoline was the main source of Pb to the atmosphere, but it now originates mostly from non-ferrous metal production (Pacyna and Pacyna, 2002). Fossil fuel combustion is the major anthropogenic source of Ni to the atmosphere. The largest anthropogenic atmospheric source of As, Cd and Zn is non-ferrous metal production. Most of these elements are released to the atmosphere as aerosol particles. Windborne particles are the main natural source for Cd, Ni, Pb and Zn. The most important natural sources of arsenic are volcanic emission and biogenic processes (Table 1.2). Anthropogenic metal emissions have diminished following the implementation of government policies (Table 1.2). For example, estimated anthropogenic Pb emissions to the atmosphere decreased from 332350 t yr^{-1} in 1983 to 11690 t yr^{-1} in 1995 (Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2002).

1.3.2 Peatlands

1.3.2.1 General information

Peatlands, or mires, are defined as soils containing more than 40 cm of peat accumulation, as opposed to mineral wetlands which have less than 40 cm of peat accumulation (NWWG, 1998).

Peatlands cover about 3% of the Earth surface and 12-20% of Canada (Tarnocai *et al.*, 2000; Charman, 2002). Figure 1.1 shows the global distribution of peatlands. Peatlands are waterlogged ecosystems in which anaerobic conditions predominate at depth. Peatlands are divided into two main types: ombrotrophic (*bogs*) and minerotrophic (*fens*). Fens are bathed by surface runoff and groundwater whose composition varies locally according to the soils, surficial sediments and base rock they percolate. Their pH is typically around 6-8 (Shotyk, 1988). Depending on the depth of the water table and the mineral composition of the water, a fen can be "poor" (oligotrophic), and relatively similar to a bog with S*phagnum* spp. dominated vegetation, or "rich" (minerotrophic) and sustain a large variety of vascular plant species. Bogs are generally convex in morphology, and their surface vegetation is isolated from the influence of minerotrophic groundwater and surface runoff. The only source of nutrients for bogs is wet and dry precipitation (Damman, 1986). The low supply of mineral particles hinders the neutralization of acids generated by the decomposition of organic matter, resulting in a low pH (around 4) environment (Shotyk, 1988).

1.3.2.2 Peatland development

Peatland development is favoured in regions where precipitation exceeds evapotranspiration (Yu *et al.*, 2010). As shown in Figure 1.1, peatlands occupy extensive areas of the northern hemisphere. Since peatlands develop in waterlogged environments, the substratum underlying these ecosystems must be nearly impermeable. A peatland is composed of two main parts: the acrotelm, corresponding to the part undergoing aerobic decomposition between the surface and the water mean table; and the catotelm, the anoxic part that is permanently waterlogged (Clymo, 1984; Clymo *et al.*, 1998). These conditions lead to slower decomposition rates than net primary production (NPP), allowing vertical and lateral aggradation of organic matter through time (Clymo, 1984; Frolking *et al.*, 1998; Vitt, 1990).

Peatlands usually form in depressions, either by terrestrialization (e.g. infilling of a lake or basin by sediments and organic material) or by paludification (i.e. waterlogging of terrestrial ecosystems). The formation of peat bogs usually begins with the infilling of shallow-water ponds or lakes (i.e. terrestrialization) (Fig. 1.2a) or previously vegetated or drier mineral ground with no aquatic stage (i.e paludification; such as the Hudson Bay peatlands) (Rydin and Jeglum, 2006). Hence, only the initiation stage of the terrestrialization and paludification processes differ, the other developmental steps are similar. With time, dying plant debris gradually accumulates underwater as fens develop. These minerotrophic peatlands are generally dominated by herbaceous species, typically *Cyperaceae,* and bryophytes (mainly brown mosses) (Fig. 1.2c). Ombrotrophic peatlands form once the peat accumulating in fens becomes isolated from the deeper groundwater. At this stage, live plant roots can no longer access nutrients in the minerotrophic groundwater and their only source is wet and dry precipitation. As mentioned earlier, the dearth of nutrients and other solutes hinders the neutralization of acids produced by the decomposition of the vegetation, thus lowering the pH. Plants species such as grasses and sedges, and typically brown mosses in general including *Scorpidium* and *Drepanocladus* cannot withstand nutrient-poor conditions and are gradually replaced by other sedges, ericaceous shrubs along with abundant *Sphagnum* mosses that are more tolerant. *Sphagnum* mosses possess a high cation exchange capacity (CEC) which allows them to exchange hydrogen ions for cations in the water and hence acidify their environment (Rydin and Jeglum, 2006). The combination of waterlogged conditions with low pH and low nutrient availability results in *Sphagnum* moss-dominated environments. Once the *Sphagnum* species take over, they maintain themselves over time given their properties (Shotyk, 1988) (Fig. 1.2d).

1.3.2.3 Peatlands as archives of atmospheric trace metal deposition

Several types of archives can be used to reconstruct the history of atmospheric metal deposition, including ice, lacustrine and marine sediments, soils and peat bogs. Most peat bogs in the Northern Hemisphere have accumulated organic material since the post-glacial ice and sea retreat, from 12,000 BP (MacDonald *et al.*, 2006), in depressed areas and over much longer periods of time in tropical regions (>20 ka; Weiss *et al.*, 2002b). As mentioned previously, ombrotrophic peat bogs are isolated from minerotrophic groundwater and therefore, unlike lake and marine sediments, do not include an important contribution from their drainage basin. Like ice sheets and glaciers, peat bogs only receive material from the atmosphere and hence can provide unadulterated records of past atmospheric trace metal deposition. Ombrotrophic peatlands are more broadly distributed than ice sheets and glaciers, they are easier to access, typically carry higher metal concentrations (of the order of $\mu g\ g^{-1}$ as opposed to $\mu g\ kg^{-1}$) because of their proximity to sources and are therefore less susceptible to sample contamination. To correctly assess the level of contamination of a sample, the pre-anthropogenic background concentration of an element needs to be known. Peat bogs can be used in this regard since several centimeters of peat will usually register accumulation over a few centuries (average accumulation rate 0.05 cm yr^{-1}) (Lavoie *et al.*, 2005).

Given the low nutrient availability, bog plants, more specifically *Sphagnum* mosses, have developed strategies to retain nutrients including metals. *Sphagnum* leaves are imbricated and spirally-arranged resulting in a high surface area for efficient trapping of atmospheric nutrients and metals (Erisman et al. 1998). Furthermore, *Sphagnum* possesses a high cation exchange capacity, allowing it to sequester cations from pore-waters (Rydin and Jeglum, 2006). The gradual decomposition of the peat material results in an increase in the concentration of humic substances, which are known for their strong metal affinity and high metal binding capacity (Rydin and Jeglum, 2006). Nevertheless, the exact mechanisms by which metals are sequestered in peat remain poorly understood and require further research.

1.3.2.4 Potential mobility of trace metals

One of the most important caveat regarding the potential use of peat bogs as archives of atmospheric metal deposition is post-depositional migration of metals (Livett, 1988; Urban, 1990; Shotyk, 1996a). To be reliable as an archive, metals should be permanently immobilized as post-depositional migration would render interpretations difficult such as in marine and lacustrine sediments.

Among all metals, lead has been most often targeted for reconstruction of its history of atmospheric deposition (Shotyk, 1996b and references therein; Bindler, 2006 and references therein; Shotyk *et al.*, 2008). It is largely recognized as being immobile despite the particularities of peat bogs (low pH, variation in redox conditions and high organic acid concentrations) (Farmer *et al.*, 1997; Shotyk *et al.*, 1998; Vile *et al.*, 1999; Weiss *et al.*, 1999; Shotyk and Le Roux, 2005).

The post-depositional behaviour of zinc differs from that of Pb and is still a matter of debate. Surface enrichment of zinc has been observed in numerous studies using peat cores, likely due to bioaccumulation by live plants (Livett *et al.*, 1979; Rausch *et al.*, 2005). Others have reported Zn to be affected by post-depositional migration (Nieminen *et al.*, 2002; Weiss *et al.* 2007; Novak and Pacherova, 2008). Zn retention can be controlled by the precipitation of sulphides under reducing conditions and by the sorption to Fe oxyhydroxides and organic matter under oxic conditions (Syrovetnyk *et al.*, 2007). In contrast, Mighall et al. (2002) proposed that Zn is immobile in ombrotrophic peat since they observed that Zn and Pb profiles were well correlated. Hence, the interpretation of Zn profiles in ombrotrophic peat cores should be made with caution. In a study of ombrotrophic peat cores from three peatlands in Finland, Frank (2005) determined that As concentration profiles closely followed those of Pb and reflected historical atmospheric deposition from mining and smelting activities. Furthermore, pore-water measurements and extraction experiments confirmed that As was largely preserved in peat bogs (Frank, 2005). Likewise, in a study of four Scottish ombrotrophic peatlands, Cloy *et al.* (2008) considered As as being immobile since its vertical profile was closely correlated with those of Sb and Pb and their distributions were consistent with those of historical atmospheric emissions. In contrast, comparisons of solid phase As and Pb profiles in three ombrotrophic peat cores collected in England revealed evidence for post-depositional mobility of As due to changes in redox conditions resulting from water table fluctuations (Rothwell *et al.*, 2009). Under waterlogged condition, As does not show post-depositional mobility (Rothwell *et al.*, 2009). Nevertheless, at sites more subject to water-table variations, As mobility may be controlled by redox cycling of Fe oxides and dissolved organic carbon (Rothwell *et al.*, 2009; Steinmann and Shotyk, 1997).

Studies of the Ni behavior in ombrotrophic peat are scarce and results are conflicting. Mobility and leaching of Ni in peat profiles was documented at a Finnish site by Ukonmaanaho *et al.* (2004). In addition to Zn, Nieminen *et al.* (2002) also reported Ni mobility in a peat profile. Likewise, Rausch *et al.* (2005) found Ni to be highly mobile in ombrotrophic peat. In contrast, Krachler *et al.* (2003) determined that Ni was mostly immobile in ombrotrophic peat but found that chemical weathering could increase Ni concentrations in minerotrophic peat. The geochemical behavior of Ni in peat bogs depends on its mineralogical associations but is also strongly dependent on pH and redox conditions of the pore-water (Nieminen *et al.*, 2008). Oxidation of Ni sulfide particles in the aerated part of the bog appears as a crucial factor in Ni retention, whereas low pH promotes dissolution of Ni oxides (Rausch, 2005). When silicates, such as clays, quartz or feldspars are the dominant Ni-bearing phases, Ni seems unaffected by post-depositional migration as these silicates are impervious to weathering even under the acidic conditions encountered in peat bogs (Le Roux, 2005).

Compared to other metals, the post-depositional behaviour of Cd in peat is poorly understood as studies are lacking. Cd was identified as being mobile in ombrotrophic peat since its vertical distribution did not reflect the impacts of smelting and mining activities at different sites in Finland (Rausch *et al.*, 2005). Cd mobility in ombrotrophic peat was also confirmed in other studies (Coggins *et al.*, 2006; Novak and Pacherova, 2008).

1.3.3 Stable lead isotopes

The isotopic composition of atmospheric Pb can be used to distinguish between natural and anthropogenic sources of Pb (Sturges and Barrie, 1987; Simonetti *et al.*, 2000; Carignan and Gariépy, 2002; Komarek *et al.*, 2008 and references therein). Lead has three radiogenic isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb) and one non-radiogenic (^{204}Pb) isotope, all naturally occurring. ^{206}Pb, ^{207}Pb and ^{208}Pb originate from the radioactive decay of ^{238}U, ^{236}U and ^{232}Th (half-lives of 4.468 Gyr, 23.5 Myr, 14.1 Gyr) respectively. The isotopic composition of rocks varies depending on their age and original U-Th-Pb composition (Doe, 1970).

Tetraethylead addition to gasoline was the main source of atmospheric Pb until its gradual phasing-out through the 1980's. Between 1982 and 1986, Struges and Barrie (1987) reported a significant difference in the isotopic composition of Pb in aerosols from the eastern U.S. (^{206}Pb/^{207}Pb ratio = ~1.213), the U.S. Midwest (~1.221) and Canada (~1.15). This difference is explained by the fact that the Pb in gasoline additives originated from different ore deposits, i.e. Bathurst ores for Canada (^{206}Pb/^{207}Pb = ~1.16) and the Mississippi Valley ores for the U.S. (^{206}Pb/^{207}Pb = ~1.30). Since the mid-1980's, this distinction became blurred as a greater variety of ores and recycled Pb were used in different industrial processes (Bollhöfer and Rosman, 2002). Nevertheless, it is still possible to use archives like peat bogs to reconstruct temporal changes in the strength of natural and anthropogenic Pb sources.

Table 1.1: Atmospheric As, Cd, Ni, Pb and Zn concentrations in remote and urban areas (ng m^{-3}). Taken from Schroeder et al. (1987).

	As	Cd	Ni	Pb	Zn
Remote areas	0.02-4	0.003-1.1	0.01-60	0.007-64	0.03-460
Urban Canada	7.7-626	2-103	4-371	353-3416	55-1390

Table 1.2: Worldwide trace metal emissions from natural and anthropogenic sources (t yr^{-1}).

Source	As	Cd	Ni	Pb	Zn
Natural sources[a]					
Windborne soil particles	0.3-5.0	0.01-0.4	1.8-20.0	0.3-7.5	3.0-35.0
Sea-salt spray	0.19-3.1	0-0.11	0.01-2.6	0.02-2.8	0.02-0.86
Volcanoes	0.15-7.5	0.14-1.5	0.93-28.0	0.54-6.0	0.31-19.0
Wild forest fires	0-0.4	0-0.22	0.1-4.5	0.06-3.8	0.3-15.0
Biogenic processes	0.39-7.5	0-1.7	0.11-1.7	0.05-3.33	0.36-16.0
Total	1.03-23.5	0.15-3.93	2.95-56.8	0.97-23.43	3.99-85.86
Anthropogenic sources[b]					
Fossil fuel combustion	809	691	86110	11690	9417
Vehicular traffic				88739	
Non-ferrous metal production	3457	2171	8878	14815	40872
Iron and steel production	353	64	36	2926	2118
Cement production	268	17	134	268	2670
Waste disposal	124	40	129	821	1933
Total	5011	2983	95287	119259	57010
1983 emissions[c]	18820	7570	55650	332350	131880

a - estimates from Nriagu (1989); b- emissions for 1995 from Pacyna and Pacyna (2002); c - from Nriagu and Pacyna (1988).

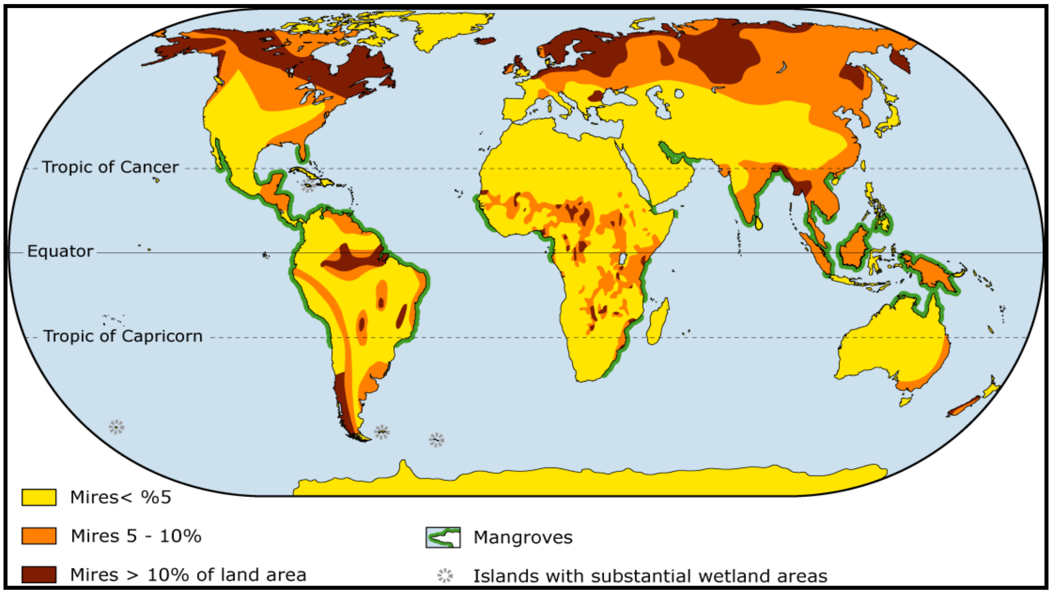


Figure 1.1: World distribution of peatlands as a proportion of land area (Charman, 2002).

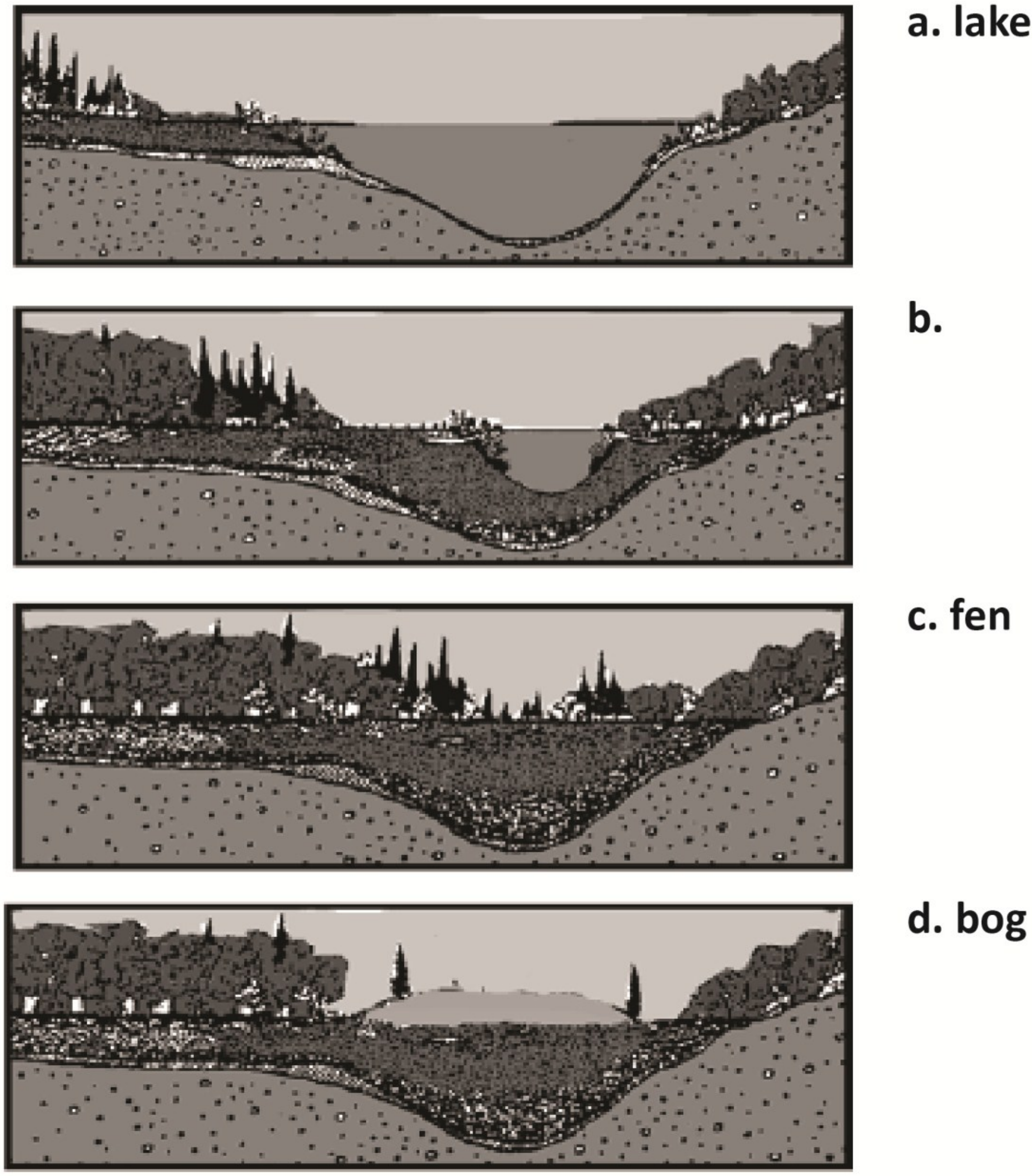


Figure 1.2: Schematic representation of peat bog development by terrestrialization process (Le Roux , 2005).

1.4 References

Alfaro-De la Torre, M., and Tessier A., 2002. Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake. *Geochim. Cosmochim. Acta*, 66, no. 20, 2549-3562.

Batonneau, Y., Bremard, C., Gengembre, L., Laureyns, J., Le Maguer, A., Le Maguer, D., Perdrix, E., and Sobanska, S., 2004. Speciation of PM_{10} sources of airborne nonferrous metals within 3-km zone of lead/zinc smelters. *Environ. Sci. Technol.*, 38, 5281-5289.

Benoît, J.M., Fitzgerald, W.F., and Damman, A.W.H., 1998. The biogeochemistry of an ombrotrophic bog: evaluation of use as an archive of atmospheric mercury deposition. *Environ. Research Sect. A*, 78, 118-133.

Bindler, R., 2006. Mired in past – looking to the future: geochemistry of peat and the analysis of past environmental changes. *Glob. Planet. Change*, 53, 209-221.

Bindler, R., Renberg, I., and Klaminder, J., 2008. Bridging the gap between ancient metal pollution and contemporary biogeochemistry. *J. Paleolimnol.*, 40(3), 755–770.

Bollhöfer, A., and Rosman, K.J.R., 2002. The temporal stability in lead isotopic signatures at selected sites in the Southern and Northern Hemispheres. *Geochim. Cosmochim. Acta*, 66, 1375–1386.

Boutron, C.F., Gorlach, U., Candelone, J.P., Bolshov, M.A., and Delmas, R.J., 1991. Decrease in anthropogenic lead, cadmium and zinc in Greenland snows since the late 1960's. *Nature*, 353, 153–156.

Boutron, C. F., Candelone, J. and Hong, S., 1995. Greenland snow and ice cores: unique archives of large-scale pollution of the troposphere of the northern hemisphere by lead and other heavy metals. *Sci. Total Environ.*, 1995, 160/161, 233-241.

Brännvall, M.-L., Bindler, R., Emteryd, O., Nilsson, M., and Renberg, I., 1997. Stable isotope and concentration records of atmospheric lead pollution in peat and lake sediments in Sweden. *Water, Air and Soil Poll.*, 100, 243–252.

Canadian Environmental Protection Act. Government of Canada, 1994. Nickel and its compounds. In Priority Substances List Assessment Report. Environment Canada and Health Canada. Ottawa, Ministry of Supply and Services. 89 p.

Carignan, J., and Gariépy, C., 1995. Isotopic composition of lichens as a tracer of the sources of atmospheric lead emissions in southern Québec, Canada. *Geochim. Cosmochim. Acta*, 59 (21), 4427-4433.

Carignan, J., Simonetti, A., and Gariépy, C., 2002. Dispersal of atmospheric lead in northeastern North America a recorded by epiphitic lichens. *Atmos. Environ.*, 36, 3759-3766.

Centeno, J.A., Mullick, M.G., Martinez, L., Page N.P., Gibb, H., Longfellow, D., Thompson, C., and Ladich, E.R., 2002. Pathology related to chronic arsenic exposure. *Environ. Health Perspect.*, 110, 883-886.

Chandramouli, K., Steer, C.D., Ellis, M., and Emond, A.M., 2009. Effects of early childhood lead exposure on academic performance and behaviour of school age children. *Arch. Dis. Child*, 94, 844-848.

Charman, D., 2002. Peatland and Environmental Change. John Wiley. pp. 301.

Chen, Y., and Ahsan, H., 2004. Cancer burden from arsenic in drinking water in Bangladesh. *Am. J. Public Health*, 94, 741-744.

Cloy, J.M., Farmer, J.G., Graham, M.C., and MacKenzie, A.B., 2008. Retention of As and Sb in ombrotrophic peat bogs: records of As, Sb and Pb deposition at four Scottish sites. *Environ. Sci. Technol.*, 43, 1756-1762.

Clymo, R.S., 1984. The limits to peat bog growth. *Philosophical Transactions of the Royal Society of London B*, 303, p 605-654.

Clymo, R.S., Turunen, J., and Tolonen, K., 1998. Carbon accumulation in peatland. *Oikos*, 81, 368-388.

Coggins, A.M., Jennings, S.G., and Ebinghaus, R., 2006. Accumulation rates of the heavy metals lead, mercury and cadmium in ombrotrophic peatlands in the west of Ireland. *Atmos. Environ.*, 40, 260-278.

Couture, R-M., Gobeil, C., and Tessier, A., 2008. Chronology of atmospheric deposition of arsenic inferred from reconstructed sedimentary records. *Environ. Sci. Technol.*, 47, 6508-6513.

Damman, A.W.H. 1986. Hydrology, development, and biogeochemistry of ombrogenous peat bogs with special reference to nutrient relocation in a western Newfounland bog. *Can. J. Bot.*, 64, 384-394.

De Vleeschouwer, F., Fagel, N., Cheburkin, A., Pazdur, A., Sikorski, J., Mattielli, N., Renson, V., Fialkiewicz, B., Piotrowska, N., and Le Roux, G., 2009. Anthropogenic impacts in North Poland over the last 1300 years – A record of Pb, Zn, Cu, Ni and S in an ombrothrophic peat bog. *Sci. Tot. Environ.*, 407, 5674-5684.

Doe, B.R., 1970. Lead Isotopes. Springer Verlag, Berlin, Heidelberg, New York, pp. 137.

Evans, G.C., Norton, S.A., Fernandez, I.J., Kahl, J.S., and Hanson, D., 2005. Changes in concentrations of major elements and trace metals in northeastern U.S.-Canadian sub-alpine forest floors. *Water, Air and Soil Poll.*, 163, 245-267.

Farmer, J.G., MacKenzie, A.B., Sugden, C.L., Edgar, J., and Eades, L.J., 1997. A comparison of the historical lead pollution records in peat and freshwater lake sediments from central Scotland. *Water, Air and Soil Poll*, 100, 253-270.

Frank, J., 2005. Determination of Arsenic and Arsenic Species in Ombrotrophic Peat Bogs from Finland. PhD Thesis, University of Heidelberg. pp. 197

Frolking, S., Bubier, J.L., Moore, T.R., Ball, T., Bellisario, L.M., Bhardwaj, A., Carroll, P., Crill, P.M., Lafleur, P.M., McCaughey, J.H., Roulet, N.T., Suyker, A.E., Verma, S.B., Waddington, J.M., and Whiting, G.J., 1998. The relationship between ecosystem productivity and photosynthetically active radiation for northern peatlands. *Glob. Biogeochem. Cycles*, 12, 115-126.

Gallon, C., Tessier, A., Gobeil, C., and Beaudin, L., 2005. Sources and chronology of atmospheric lead deposition to a Canadian Shield lake: inference from Pb isotopes and PAH profiles. *Geochim. Cosmochim. Acta*, 69, no. 13, 3199-3210.

Gallon, C., Tessier, A., and Gobeil, C., 1996. Historical perspective of industrial lead emissions to the atmosphere from a Canadian smelter. *Environ. Sci. Technol.*, 40, 741-747.

Gélinas, Y., Lucotte, M., and Schmidt, J., 2000. History of the atmospheric deposition of major and trace elements in the industrialized St. Lawrence Valley, Quebec, Canada. *Atmos. Environ.*, 34, 1797-1810.

Givelet, N., and Roos-Barraclough, F., 2003. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural "background" values (past 8000 years). *J. Environ. Monit.*, 5(6), 935–949.

Gobeil, C., Johnson, W.K., MacDonald, R., and Wong, C.S., 1995. Sources and burden of lead in St. Lawrence Estuary sediments: isotopic evidence. *Environ. Sci. Technol.*, 29, 193-201.

Kada, J., and Heit, M., 1992. The inventories of anthropogenic Pb, Zn, As, Cd, and the radionuclides ^{137}Cs and excess ^{210}Pb in lake sediments of the Adirondack region, USA. *Hydrobiologia*, 246, 231-241.

Kettles, I.N., and Bonham-Carter, G.F., 2002. Modelling dispersal of metals from a copper smelter at Rouyn-Noranda (Québec, Canada) using peatland data. *Geochemistry: Exploration, Environment, Analysis*, 2, 99-110.

Krachler, M., Mohl, C., Emons, H., and Shotyk, W., 2003. Atmospheric deposition of V, Cr and Ni since the Late Glacial: effects of climatic cycles, human impacts, and comparison with crustal abundance. *Environ. Sci. Technol.*, 37, 2658-2667.

Kylander, M.E., Weiss, D.J., and Kober, B., 2009. Two high resolution terrestrial records of atmospheric Pb deposition from New Brunswick, Canada, and Loch Laxford, Scotland. *Sci. Tot. Environ.*, 407, 1644–1657.

Lavoie, M., Paré, D. and Bergeron, Y., 2005. Impact of global change and forest management on carbon sequestration in northern forested peatlands. *Environ. Rev.*, 13, 199-240.

Le Roux, G., Weiss, D., Grattan, J., Givelet, N., and Krachler, M., 2004. Identifying the sources and timing of ancient and medieval atmospheric lead pollution in England using a peat profile from Lindow bog, Manchester. *J. Environ. Monit.*, 6 (5), 502-510.

Le Roux, G., 2005. Fate of natural and anthropogenic particles in peat bogs. Ph.D. Thesis, University of Heidelberg, Heidelberg, pp. 1-217.

Livett, E. A., Lee, J. A., and Tallis, J. H., 1979. Lead, zinc and copper analyses of British blanket peats. *J. Ecol.*, 67, 865-891.

Livett, E.A., 1988. Geochemical monitoring of atmospheric heavy metal pollution: theory and application. *Adv. in Ecol. Res*., 18, 65-177.

Lucotte, M., Mucci, A., Hillaire-Marcel, C., Pichet, P., and Grondin, A., 1995. Anthropogenic mercury enrichment in remote lakes of Northern Québec (Canada). *Water, Air and Soil Poll.*, 80, 467-476.

MacDonald, G.M., Beilman, D.W., Kremenetski, K.V., Sheng, Y., Smith, L.C., and Velichko, A.A., 2006. Rapid early development of circumarctic peatlands and atmospheric CH_4 and CO_2 variations. *Science*, 314, 285-288.

Mighall, T.M., Abrahams, P.W., Grattan, J.P., Hayes, D., Timberlake, S., and Forsyth, S., 2002. Geochemical evidence of atmospheric pollution derived from prehistoric copper mining at Copa Hill, Cwmystwyth, mid-Wales, UK. *Sci. Tot. Environ.*, 292, 69–80.

National Wetland Working Group, 1988. *Wetlands of Canada*. Ecological land classification series No. 24. Sustainable development branch, Environment Canada, Ottawa, and Polyscience Publications, Montreal, 452.

Nieminen, T.M., Ukonmaanaho, L., and Shotyk, W., 2002. Enrichments of Cu, Ni, Zn, Pb and As in an ombrothrophic peat bog near a Cu–Ni smelter in Southwest Finland. *Sci. Tot. Environ.*, 292, 81–89.

Nieminen, T.M., Ukonmaanaho, L., Rausch, N., and Shotyk, W., 2008. Biogeochemistry of nickel and its release into the environment. *Met. Ions Life Sci,*. 2, 1-30.

Nigg, J.T., Knottnerus, G.M., Martel, M.M., Nikolas, M., Cavanagh, K., Karmaus, W., and Rappley, M.D., 2008. Low blood lead levels associated with clinically diagnosed attention-deficit/hyperactivity disorder and mediated by weak cognitive control. *Biol. Psychiatry*, 63, 325-331.

Norton, S.A., Evans, G.C., and Kahl, J.S., 1997. Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath Bog and to nearby Sargent Mt. Pond, Maine, USA. *Water, Air and Soil Pollu.*, 100, 271–286.

Novak, M., and Pacherova, P., 2008. Mobility of trace metals in pore waters of two Central European peat bogs. *Sci. Tot. Environ.*, 394, 331–337.

Nriagu, J.O., and Pacyna, J.M., 1988. Quantitative assessment of of worldwide contamination of of air water and soils by trace metals. *Nature*, 333, 134-139.

Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals. *Nature*, 338, 47-49.

Ouellet, M., and Jones, H., 1983. Paleolimnological evidence for the long-range atmospheric transport of acidic pollutants and heavy metals into the Province of Quebec, eastern Canada. *Can. J. Earth Sci.*, 20, 23-36.

Pacyna, J.M., and Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.*, 9, 269-298.

Rahn, K.A., 1976. *The Chemical Composition of Atmospheric Aerosol*, Technical Report, Graduate School of Oceanography, University of Rhode Island. pp. 265.

Rausch, N., Nieminen, T.M., Ukonmaanaho, L., Le Roux, G., Krachler, M., Cheburkin, A., Bonani, G., and Shotyk, W., 2005. Comparison of atmospheric deposition of copper, nickel, cobalt, zinc, and cadmium recorded by Finnish peat cores with monitoring data and emission records. *Environ. Sci. Technol.*, 39, 5989–5998.

Rausch, N., 2005. Deposition and fate of trace metals in Finnish bogs and implications for the use of bogs as geological archives. Ph. D. Thesis, University of Heidelberg, Heidelberg, pp. 1-203.

Roos-Barraclough, F., Givelet, N., Cheburkin, A.K., Shotyk, W., and Norton, S.A., 2006. Use of Br and Se in peat to reconstruct the natural and anthropogenic fluxes of anthropogenic Hg: a 10000- years record from Caribou bog, Maine. *Environ. Sci. Technol.*, 40, 3188–3194.

Rothwell, J.J., Taylor, K.G., Ander, E.L., Evans, M.G., Daniels S.M., and Allott, T.E.H., 2009. Arsenic retention and release in ombrotrophic peatlands. *Sci. Tot. Environ.*, 407, 1405-1417.

Rydin, H. and Jeglum, J. K., 2006. The Biology of Peatlands, Oxford University Press, Oxford, 360 pp.

Schroeder, W.H., Dobson M., Kane D.M., and Johnson, N.D., 1987. Toxic trace elements associated with airborne particulate matter: a review. *J. Air Pollut. Control Assoc.*, 37 (11), 1267-1285.

Shotyk, W., 1988. Review of the inorganic geochemistry of peats and peatland waters. *Earth Sci. Rev.*, 25, 95-176.

Shotyk, W., 1996a. Natural and anthropogenic enrichment of As, Cu, Pb, Sb and Zn in ombrothrophic versus minerotrophic peat bog profiles, Jura Mountains, Switzerland. *Water, Air and Soil Poll.*, 90, 375-405.

Shotyk, W., 1996b. Peat bogs archives of atmospheric metal deposition: geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. *Environ. Rev.*, 4, 149-183.

Shotyk W., Weiss, D., Appleby, G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., and van Der Knaap, W.O., 1998. History of atmospheric lead deposition since 12,370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland. *Science*, 281, 1635–1640.

Shotyk, W., and Le Roux, G., 2005. Biogeochemistry and cycling of lead. In: Sigel, A., Sigel, H., Sigel, R.K.O., editors. Biogeochemical Cycles of the Elements. Metal Ions in Biological Systems. New York: M. Dekker, 240–275.

Shotyk, W., and Krachler, M., 2010. The isotopic evolution of atmospheric Pb in central Ontario since AD 1800, and its impacts on the soils, waters, and sediments of a forested watershed, Kawagama Lake. *Geochim. Cosmochim. Acta*, 74, 1963-1981.

Simonetti, A., Gariépy, C., and Carignan, J., 2000. Pb and Sr isotopic evidence from sources of atmpsheric heavy metals and their deposition budget in northeastern North America. *Geochim. Cosmochim. Acta*, 64 (20), 3439-3452.

Steinmann, P., and Shotyk, W., 1997. The pH, redox chemistry, and speciation of Fe and S in pore waters from two contrasting Sphagnum bogs, Jura Mountains, Switzerland. *Geochim. Cosmochim. Acta*, 61, 1143–63.

Steinnes, E., and Friedland, A.J., 2006. Metal contamination of natural surface soils by long-range atmospheric transport: existing and missing knowledge. *Environ. Rev.*, 14, 169-186.

Sturges, W.T., and Barrie, L.A., 1987. Lead 206/207 isotope ratios in the atmosphere of North America as tracers of US and Canadian emissions. *Nature*, Vol. 329, 144-146.

Syrovetnik, K., Malmstrom, M. E. and, Neretnieks, I., 2007. Accumulation of heavy metals in the Oostriku peat bog, Estonia: determination of binding processes by means of sequential leaching. *Environ. Pollut.* 2007, 147, 291–300.

Tarnocai, C., Kettles, I.M., and Lacelle, B., 2002. *Peatlands of Canada Database.* Geological Survey of Canada Open File 4002. Ottawa: Natural Resources Canada.

Telmer, K., Bonham-Carter, G.F., Kliza, D.A., and Hall, G.E.M., 2004. The atmospheric transport and deposition of smelter emissions: evidence from the multi-element geochemistry of snow, Quebec, Canada. *Geochim. Cosmochim. Acta*, 68 (14), 2961-2980.

Ukonmaanaho, L., Nieminen, T., Rausch, N., and Shotyk, W., 2004. Heavy metal and arsenic profiles in ombrogenous peat cores from four differently loaded areas in Finland. *Water, Air and Soil Poll.*, 58, 277–294.

Urban, N.R., Eisenreich, S.J., Grigal, D.F., and Schurr, K.T., 1990. Mobility and diagenesis of Pb and ^{210}Pb in peat. *Geochim. Cosmochim. Acta*, 54**,** 3329-3346.

US EPA, 1982, *An exposure and risk assessment for arsenic*. EPA 440/4-85-005. Washington, DC, US Environmental Protection Agency.

Vile, M.A., Wieder, R.K., and Novak, M., 1999. Mobility of Pb in Sphagnum-derived peat. *Biogeochemistry*, 45, 35-52.

Vitt, D.H., 1990. Growth and production dynamics of boreal mosses over climatic, chemical, and topographical gradients. *Botanical Journal of the Linnean Society*, 104, 35-59.

Weiss, D., Shotyk, W., Appleby, G., Kramers, J.D., and Cheburkin, A.K., 1999. Atmospheric Pb deposition since the Industrial Revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environ. Sci. Technol.*, 33, 1340-1352.

Weiss, D., Shotyk, W., Boyle, E.A., Kramers, J.D., Appleby, G., and Cheburkin, A.K., 2002a. Comparative study of the temporalevolution of atmospheric lead deposition in Scotland and eastern Canada using blanket peat bogs. *Sci. Tot. Environ.*, 292, 7-18.

Weiss, D., Shotyk, W., Rieley, J., Page, S., Gloor, M., Reese, S., and Martinez-Cortizas, A., 2002b. The geochemistry of major and trace elements in a forested peat bog, Kalimatan, SE, Asia, and its implacations for past atmospheric dust deposition. *Geochim. Cosmochim. Acta*, 66(33), 2307-2323.

Yu, Z., Loisel, J., Brosseau, D.P., Beilman, D.W., and Hunt, S.J., 2010. Global peatland dynamics since the Last Glacial Maximum. *Geophysical Research Letter*, 37, 1-5.

Chapter 2: History of atmospheric trace metal deposition along the St. Lawrence Valley (Quebec) using peat bog records

2.1 Introduction

Human activities have affected the global and regional geochemical cycles of several toxic elements such as Pb, Cd, Hg, with potentially important repercussions on ecosystems and adverse effects on human health (Nriagu and Pacyna, 1988). This large-scale contamination is recorded in various natural archives such as ice cores, lacustrine and marine sediments and peat bogs and extends back several thousands of years in certain cases (Boutron *et al.*, 1991, 1995; Shotyk *et al.*, 1996, 2002; Krachler *et al.*, 2009).

Peat bogs are proving to be valuable archives of atmospheric trace metal deposition (Weiss *et al.*, 1999a; Bindler, 2006). In ombrotrophic peatlands (peat bogs), the surface vegetation is fed exclusively by nutrients delivered by wet and dry deposition from the atmosphere (Damman, 1986; Shotyk, 1988), as they are isolated from the influence of groundwater and surface runoff. Assuming that most metals deposited on the surface of ombrotrophic bogs are immobile, peat bogs can be used to reconstruct the history of atmospheric trace metal deposition.

In contrast to the extensive amount of work carried out in Europe on the reconstruction of atmospheric metal deposition using peat bogs (Brännvall *et al.*, 1997; Shotyk *et al.*, 1998; Bindler *et al.*, 2008), few similar studies have been conducted in North America. Most of the latter focused either on Hg (Benoit *et al.*, 1998; Givelet *et al.*, 2003; Roos-Barraclough *et al.*, 2006) or Pb (Norton *et al.*, 1997; Weiss *et al.*, 2002; Kylander *et al.*, 2009; Shotyk and Krachler, 2010). A number of studies, using archives other than peat bogs, were undertaken in eastern North America, and focused on other metals such as As, Cd and Zn (Kada and Heit, 1992; Gélinas *et al.*, 2000; Alfaro-De la Torre and Tessier, 2002; Couture *et al.*, 2008).

The St. Lawrence Valley (SLV) is a natural wind corridor, oriented from the south-west to the north-east, carrying contaminants from the mid-western Great Lakes region to the Atlantic Ocean (Figure 2.1). The western portion of the SLV is fairly industrialized and urbanized, encompassing the cities of Ottawa and Montreal. A decreasing gradient of atmospheric deposition away from major metal-emitting sources, particularly the United States' NE, is well documented (Ouellet and Jones, 1983; Carignan and Gariépy, 1995; Lucotte *et al.*, 1995; Simonetti *et al.*, 2000; Evans *et al.*, 2005). For these reasons, the St. Lawrence Valley is well suited for studies of long-range trace metal atmospheric transport.

In this study, we present historical records (focusing on 1800 AD to the present) of elemental enrichment factors and accumulation rates for As, Cd, Ni, Pb, and Zn based on their analysis in the top meter of three ombrotrophic peat bog cores collected along the St. Lawrence Valley from Ottawa to Baie-Comeau. ^{210}Pb analyses were combined with radiocarbon dating to build age-depth models for each of the peat profiles. In addition, other metals were analyzed to characterize the trophic status of the bogs, their mineral matter content, and to identify processes (redox, bioaccumulation) responsible for metal remobilization. Finally, the stable isotopic composition of the Pb was determined to identify potential anthropogenic and natural sources.

2.2 Material and methods

2.2.1 Study sites

The Mer Bleue bog (45°41'N, 75°48'W; 28 km^2) is a Provincial Conservation area situated 10 km east of Ottawa (Fig. 2.1). The climate of the region is characterized by a mean annual temperature of 6±0.8°C and annual precipitations of 943±34 mm fairly evenly spread through 12 months. Lowest and highest monthly temperatures of -10.8±2.9°C and 20.9±1.1°C are recorded in January and July, respectively (Environment Canada, 2011). The Mer Bleue bog developed ca. 8500 years ago in a postglacial channel carved into the silty-clay sediments of the

Champlain Sea, covering the limestone substrate, with peat thickness of 5 to 6 m at its center (Roulet *et al.*, 2007). The selected coring site is in a slightly domed area (Joyal, 1970) with surface microtopography expressed in a subtle low hummock/hollow pattern and covered by Ericaceae (*Chamaedaphne calyculata*, *Ledum groenlandicum*, *Kalmia angustifolia*) and *Sphagnum* mosses mainly *S. capillifolium and S.fuscum* (Moore *et al.*, 2002).

The Mirabel peatland (45°41'N, 74°02'W; 2.15 km^2) is located 35 km northwest of Montreal in the St. Lawrence lowlands near the Mirabel international airport (Fig. 2.1). The regional climate is characterized by abundant precipitations fairly evenly distributed through the year (annual mean: 1064±36 mm). The average annual mean temperature is 5±1.2°C with monthly averages of 19.5±0.9°C in July and -12.1±3.1°C in January (Environment Canada, 2011). The Mirabel peatland is a bog which developed in a former proglacial channel of the Champlain Sea. The site lies over silty-clay marine sediments deposited above a till on sandstone-dolomitic bedrock (Laverdière, 1972). This peatland is also characterized by a surface microtopography of subtle low hummock/hollow pattern. The core was retrieved from an area of the peatland dominated by *Sphagnum capillifolium* and *Chamaedaphne calyculata* with some *Sphagnum magellanicum*, *Kalmia angustifolia* and *Rhododendron groelandicum* (Muller *et al.*, 2003). Peat thickness near the coring site is about 3.3 m and a basal date of 10 030 yr cal. BP was obtained by Muller *et al.* (2003). Further details about the vegetation, morphometry and the development of Mirabel bog can be found in Muller *et al.* (2003).

The Baie peatland (49°04'N, 68°14'W; 1.5 km^2) is located 20 km southwest of Baie-Comeau, at the eastern end of the Lower St. Lawrence Estuary (Fig. 2.1). Annual temperature averages 1.5±0.9°C, with monthly means of -14.4±2.2°C in January and 15.6±0.9°C in July. The annual precipitation is 1014±39 mm, 362±16 mm of which falls as snow (Environment Canada, 2011). The Baie bog is an ombrotrophic complex situated in the southwestern section of a peatland complex in Pointe-Lebel. The peatland developed over marine-clay sediments covering gneiss and paragneiss (Bernatchez, 2003). Maximum peat thickness at the centre is 4.5 m and a basal date of 4210 yr cal BP was determined by G. Magnan (pers. comm.).The site is dominated by *Sphagnum fuscum and S. rubellum* in the bryophyte assemblage, ericaceous shrubs (*Chamaedaphne calyculata* and *Kalmia angustifolia* L.) and sparse dwarf *Picea mariana*. This peatland is characterized by a well-defined surface hummock/hollow microtopography with a mean water table (MWT) of approximately 25-30 cm below the surface.

2.2.2 Coring and sample preparation

One peat core was collected using cylindrical a PVC pipe (10 cm i.d. x100 cm long) at the Mirabel site and a stainless steel box corer (8x8x100 cm) (Jeglum, *et al.*, 1991) at the Baie and Mer Bleue sites. The cores collected using the box corer were taken out of the corer, wrapped in a plastic film, and stored in plastic boxes, whereas the one collected using the PVC pipe was extruded while frozen in the laboratory. All cores were kept in a refrigerator at 4°C. The cores were cut in the laboratory at 1-cm intervals using a serrated ceramic knife. The core edges (1 cm) were removed from each subsample to avoid contamination by the corer. The remaining samples were freeze-dried and ground using a Pulverisette® agate mortar grinder. The mortar was cleaned with ethanol between each sample, rinsed with Milli-Q water, and air-dried. Bulk density was measured at every centimeter from 3 cm^3 subsamples of fresh peat collected using a calibrated 1-cm^3 cutting ring. Subsamples were weighted fresh and after drying at 105°C overnight. Ash content was obtained by loss on ignition of subsamples at 550°C for 4 hours (modified from Heiri *et al.*, 2001). The residues of ignition are assumed to be ash and mineral particles like clay or sand.

2.2.3 Trace metal analysis

Powdered peat samples (0.1 g) were acid-digested in Teflon beakers. The acid digestion was carried out in two steps on a hotplate with evaporation to dryness between each step using a mixture of 2 ml of HNO_3 and 0.5 ml of HF for mineral matrix dissolution and 1 ml H_2O_2 for the oxidation of the organic matter (Le Roux and De Vleeschouwer, 2010). After the last step, the solid residue was dissolved in 30 ml of 2% HNO_3. All reagents used were Optima® grade from Fisher Scientific. Metal concentrations were determined using an Agilent 7500ce ICP-MS (Dept. Chemistry and Biochemistry, Concordia University, Canada). Fe concentrations were measured, in the same solutions, using a Perkin Elmer AAnalyst 100 Flame atomic adsorption spectrometer (Dept. Earth and Planetary Sciences, McGill University, Montreal). Calibrations were made using external certified reference solutions (SCP Science) of the elements of interest. The analytical precision was determined by replicate analysis of three international reference materials: NIST SRM 1515 apple leaves, SRM 1547 peach leaves and SRM 1575A pine needles. Detection limits, accuracy and reproducibility are reported in Table 2.1.

2.2.4 Lead isotope ratios

The stable isotopic composition of atmospheric Pb deposits reflects the isotopic signature of its source ore, providing an effective tool to discriminate its origin (Sturges and Barrie, 1987; Komárek *et al.*, 2008 and references therein). The concentrations of the following stable lead isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, were determined to identify its sources. Stable lead isotopic ratios were measured on samples taken at 1 to 5-cm intervals from the Baie and Mer Bleue cores. Samples from the deeper part of each core were also analyzed (section 2.4). About 50 mg of powdered sample were acid-digested in two steps 1) *aqua regia* for 24h and 2) 1 ml of HNO_3 + 0.25 ml of HF for 24h. Samples were evaporated to dryness after each step. Residues were dissolved in 2 ml of 0.8 N HBr prior to chromatographic separation. All acids were sub-boiled twice. Chromatographic separation was performed by double elution through preconditioned anionic exchange columns (AG1X8) by successive HCl and HBr additions following a modified protocol described by Manhès *et al.* (1978). The eluted solution was evaporated and dissolved in 0.5 ml of 2% HNO_3.

Stable lead isotopic ratios were measured on a Nu Plasma II MC-ICP-MS at the Laboratoire de géochimie des isotopes radiogéniques at GEOTOP-UQAM in Montreal. The mass bias was corrected using the thallium doping technique and by normalizing the Tl isotopic value by repeated analysis of the NBS-981 (n=12) standard which yielded: $^{206}Pb/^{204}Pb = 16.9380 \pm 0.0029$; $^{207}Pb/^{204}Pb = 15.4945 \pm 0.0055$; $^{208}Pb/^{204}Pb = 36.7087 \pm 0.0181$; $^{207}Pb/^{206}Pb = 0.9148 \pm 0.0002$; $^{208}Pb/^{206}Pb = 2.1672 \pm 0.0007$. A detailed description of the stable Pb isotope measurement technique can be found in Poirier *et al.* (2004). Pb blanks were lower than 150 pg and negligible as they were contributing to less than 0.6%.

2.2.5 Chronology

2.2.5.a ^{210}Pb dating

The activity of ^{210}Pb was determined by measuring the decay of its granddaughter product ^{210}Po by alpha spectrometry. Polonium was extracted from ca. 0.1-0.4 g of powdered peat using a sequential HNO_3-HCl-HF-H_2O_2 digestion before electro-deposition on silver discs (Hamilton and Smith, 1986). Samples were spiked with a known amount of ^{209}Po to evaluate the chemical extraction efficiency. The ^{209}Po and ^{210}Po activities were measured with an EGG Ortec 476A alpha spectrometer, equipped with a Si surface barrier semiconductor detector coupled to the MAESTRO software for data acquisition. ^{210}Pb analyses were carried out at the Laboratoire de radiochronologie at GEOTOP-UQAM in Montreal.

The excess (unsupported) ^{210}Pb activity was calculated by subtracting the supported ^{210}Pb activity from the total measured activity. The supported ^{210}Pb activity is assumed to be constant through the profile and assessed from the ^{210}Pb activity in the deeper core samples dated by ^{14}C AMS. The measurement uncertainties (Tables 2.2-2.4; Fig. 2.2), corresponding to one-sigma, were calculated from counting statistics. The constant rate of supply (CRS) model was applied to calculate the age of the peat layers (Appleby and Oldfield, 1978).

2.2.5.b ^{137}Cs

Since ca. 1952 AD, thermonuclear weapons testing released anthropogenic radionuclides, including ^{137}Cs, to the atmosphere and these were rapidly deposited onto the land surface (Davis *et al.*, 1984). ^{137}Cs peaks are usually recorded in the sediments ca. 1963 AD and ca. 1986 AD, corresponding to the peak period of emissions from nuclear weapons testing and the Chernobyl nuclear plant accident, respectively. To confirm the age model obtained from ^{210}Pb, ^{137}Cs activity was measured using its gamma emission at 662 kEv in 10 cubic centimeters of dry, powdered peat samples from selected depths in the Baie and Mirabel peat cores (Appendix 2). A high purity germanium well detector (Canberra GCW3522-type) was used at the Laboratoire de radiochronologie at GEOTOP-UQAM in Montreal. To account for self-absorption of gamma ray, a plant radionuclide standard (CLV-1, Canmet, Ottawa), composed of spruce twigs and needles, from the Cluff Lake mining area, was used to calibrate the detector efficiency at 662 kEv.

2.2.5.c ^{14}C dating

Terrestrial macrofossils were selected in two to five subsamples per core after soaking in Milli-Q water, to separate macrofossils from degraded material, and transferred to a Petri dish (Mauquoy *et al.*, 2004). This method allows selecting only the aboveground parts of the plant and hence prevents contamination by young carbon from rootlets. When possible, macrofossils collected for dating were *Sphagnum* stems as they yield more reliable ^{14}C dates (Nilsson *et al.*, 2001). When *Sphagnum* remains were not present in sufficient quantities, charred *Picea* needles and charcoal fragments were selected (Table 2.5). Radiocarbon measurements were carried out at the Keck-CCAMS facility (Irvine, U.S.A.). Age intervals were obtained by using the InterCal09 calibration curve (Reimer *et al.*, 2009) in the Clam software (Blaauw, 2010).

2.2.6 Metal enrichment factors

Metals enrichment factors (E.F.) (Appendix 1) were calculated in order to differentiate anthropogenic from natural metal inputs to the peat (Shotyk *et al.*, 2002). Sc was used as a reference element because its mineral phases are resistant to alteration (Shotyk *et al.*, 2002). Metal enrichment factors were calculated as follows:

(1) $$E.F. = ([E]_{sample}/[Sc]_{sample})/([E]_{lithogenic}/[Sc]_{lithogenic})$$

where E.F. is the enrichment factor, $[E]_{sample}$ is the sample's concentration of the element of interest, $[Sc]_{sample}$ is the concentration of Sc in the sample, $[E]_{lithogenic}$ is the mean concentration of the element in the earth's crust and $[Sc]_{lithogenic}$ is the concentration in Sc in the crust. Upper Continental Crust reference values are 14.8, 65, 56, 1.7, 0.1, 16 and 4010 µg g^{-1} respectively for Pb, Zn, Ni, As, Cd and Sc (Wedepohl, 1995). Sc was used as well to estimate the concentration of lithogenic elements deposited from the atmosphere using equation 2. The anthropogenic element concentrations were calculated by equation 3.

(2) $$[E]_{lithogenic} = [Sc]_{sample} * (\frac{[E]}{[Sc]})_{lithogenic}$$

where:

(3) $$[E]_{anthropogenic} = [E]_{total} - [E]_{lithogenic}$$

2.3. Results

2.3.1 Chronologies

Cores chronologies are based on ^{210}Pb and radiocarbon dating (Tables 2.2-2.5; Fig. 2.2). The activity of unsupported ^{210}Pb approaches zero below 40 cm in the

Baie core and at approximately 50 cm in the Mer Bleue and Mirabel cores (Fig. 2.2). Results show important differences in peat accumulation rates over time, as indicated by deviations from the typical exponential decay curves of ^{210}Pb. This is especially noteworthy in the Mer Bleue core where the ^{210}Pb peaks correspond to two charcoal horizons (42 and 46 cm) which render part of the ^{210}Pb profile unreliable. These charcoal horizons correspond to undocumented, important on-site fire events as charcoal fragments are greater than 2 mm and charred *Picea* needles were abundant. These fires likely generated net peat loss and, hence, negative accumulation rates.

In an attempt to constrain the ^{210}Pb chronologies, ^{137}Cs measurements were made on the Baie and Mirabel cores. The ^{137}Cs profiles cannot confirm or infirm the age-depth models obtained from ^{210}Pb as they clearly show post-depositional remobilization of Cs since the ^{137}Cs peaks are much deeper than expected and the activities are high even outside of the bomb testing period (Appendix 2). Nevertheless, the ^{210}Pb chronology in the Baie core is consistent with the rate of accumulation and the date (~1875 AD) obtained at 32 cm depth derived from a ^{14}C measurement (Table 2.2 and 2.5). At this site, the core covers a period of approximately 1000 years (Table 2.5). A spline curve with a smoothing factor of 0.3 was used to fit the age-depth model (Fig. 2.2).

The 61-cm long Mirabel bog core does not record as long a period of time as the two other cores and likely extends further than the Industrial era (older than the 17th century) with a calibrated radiocarbon age date of ~1810 AD at 48 cm (1677-1933, Table 2.5). As peat was very decomposed between 48 and 61 cm, no datable material was found, explaining the absence of an age-depth model for the deeper part of this core.

For the three sites, many of the ^{14}C dates fall in the gap between the oldest reliable ^{210}Pb dates (ca. 1850 AD) and the first reliable ^{14}C dates (ca. 17th century) (Taylor, 1997). Because the Mer Bleue core was compressed by an estimated 12 cm during coring, the age-depth model was adjusted using the ^{206}Pb/^{207}Pb profile. For example, the probability distribution of the calibrated date at 63 cm shows that two age-dates are possible. Both ages could lie on the age-depth curve, but the youngest one (1790 AD) was deemed most reliable given that, in several studies carried out in this region, a decrease in the $^{206}Pb/^{207}Pb$ starting between 1800 and 1850 AD was reported (Gallon et al., 2005; Graney et al., 1995; Shotyk and Krachler, 2010). Being reasonably close to the other study sites, we assumed that the $^{206}Pb/^{207}Pb$ profile in the Mer Bleue core covers the same period (Fig 2.7). The Mirabel core was compressed by an estimated 7 cm, but could not be adjusted since no stable Pb isotope analyses were carried out on this core.

For the past 200 years, the Mirabel and Mer Bleue cores show higher peat accumulation rates (0.24 and 0.29 cm respectively) than the Baie bog (0.19 cm yr^{-1}). Nevertheless, when considering the whole length of the peat cores, net accumulation over the last millennium is higher in the Baie bog (0.09 cm yr^{-1}) than the Mer Bleue bog (0.06 cm yr^{-1}). The dated section of the Mirabel core was not long enough (~49 cm) to derive accumulation rates over more than the last 200 years.

2.3.2 Trophic status of the peatlands

Peatlands must be ombrotrophic to be reliable archives of atmospheric trace metal deposition, i.e., the only source of nutrients should come from atmospheric deposition. The trophic status (*i.e.* the source of nutrients) of a peatland should be confirmed before its record can be properly interpreted since, otherwise, trace metals and nutrients may be supplied to the peatland by diffusion following mineral weathering at the base of the peat deposit. The core vegetation assemblages are typical of ombrotrophic peatlands (*Sphagnum* and/or Ericaceous stems and rootlets) at the three sites. This ombrotrophic assemblage is also present throughout each profile except for a section of the Mirabel core, where highly decomposed ligneous peat is present between 49 and 61 cm. Furthermore, the ash content at each site is usually lower than 4% (Fig 2.3), typical of ombrotrophic bogs (Shotyk *et al.*, 2001). The Sr and Ca concentrations can also be used to assess the trophic status of a peatland, as these elements are typically supplied by mineral weathering and diffuse upward in the peat column. Low Sr (< 20 ppm) and Ca (< 4000 ppm or 0.4%) concentrations are typical of ombrotrophic bogs (Shotyk *et al.*, 2001). Ca concentrations average 0.02±0.02, 0.19±0.03 and 0.25±0.03% and Sr concentrations 13.3±7.0, 13.3±5.1 and 13.6±7.1 μg g^{-1} in the Baie, Mirabel and Mer Bleue cores, respectively (Fig 2.3), which further confirms the ombrotrophy of the cores. Sr concentration peaks (above 30 μg g^{-1}) correspond to peaks in bulk density and/or Sc concentrations (Fig. 2.3), as well as very decomposed horizons, often containing charcoal remnants, suggesting decreased peat accumulation, increased decomposition or fires rather than a minerogenic origin (Fig. 2.3). In most cases, these horizons also registered peaks in all other elements measured.

2.3.3 Element concentration profiles

Each core displays a unique Pb concentration profile with depth (Fig. 2.4). Lead concentrations are lowest at the top and bottom of the cores, but the former are generally one order of magnitude higher than the latter (pre-industrial). Maximum Pb concentrations are found at intermediate depths, but their position and assigned chronologies differ in each core: 320 μg g^{-1} (~1946) in the Baie bog core, 120 μg g^{-1} (~1964) in the Mirabel bog core, and 97 μg g^{-1} (~1915) in the Mer Bleue bog core. Nevertheless, the increase in Pb concentrations in each core is coincident with the beginning of the 19th century. The arsenic and cadmium concentration profiles are similar to those of lead, as their maxima are found around the same depth, with peaks of 2.2, 4.9 and 5.4 μg g^{-1} of As and 0.4, 1.9 and 1.0 μg g^{-1} of Cd in the Baie, Mirabel and Mer Bleue cores, respectively. The nickel concentration profile exhibits high variability in the Baie bog core, but is similar to the other elements (Pb, As, Cd) in the Mirabel and Mer Bleue bog cores. Zinc concentration profiles differ significantly between sites. In the Baie bog core, Zn concentrations are highly variable, but similar to those of Ni. Zn concentrations vary between 10 and 40 μg g^{-1} in the upper half of the core, and are generally lower than 12 μg g^{-1} in the lower half. The higher Zn concentrations roughly correspond with high As, Cd and Pb concentrations. The highest Zn concentration in the Mirabel core is found at the top of the core (295 µg g^{-1} at 0.5 cm depth). In the Mer Bleue core, the Zn concentration profile resembles those of the other metals with lower concentrations at the top and bottom of the core and a zone of high concentrations and multiple peaks between 20 and 60 cm depth. With the exception of Pb, metal concentrations are generally higher in the Mer Bleue and Mirabel bog cores than in the Baie bog core.

2.3.4 Accumulation rates

Metal accumulation rates (µg or mg m^{-2} yr^{-1}), as surrogate estimates of the atmospheric deposition rates, were calculated as follows:

$$\text{(4)} \qquad \mathrm{AR} = [M] \times \delta \times PA$$

where [M] is the total metal concentration (µg g^{-1}), δ is the peat bulk density (g cm^{-3}) and PA is the peat accumulation rate (cm yr^{-1}). The use of accumulation rates (AR) instead of concentrations or enrichment factors is more appropriate, as variations in net peat accumulation and humification are taken into account and, hence, allows for a direct comparison of the core records. Figure 2.5 displays the AR of the targeted metals during the last two centuries and shows that metal deposition rates increase from 1810-1850 in the three cores. The ARs in the Mirabel and Mer Bleue cores display a bimodal distribution, i.e. a large increase in the 1940's and a second stronger peak in the late 1960's to early 1970's. The AR maxima in the 1940's are generally of the same order at the two sites while the second peak in the Mer Bleue core is higher for all metals. With the exception of Pb, metal accumulation rates are generally more than one order of magnitude lower in the Baie core and, thus, patterns are not readily discernible in this core. Pb ARs are highest in 1951 and during the 1960's in the Baie core. In the Mirabel core, the Zn ARs are at their maximum in the youngest samples.

2.3.5 Stable lead isotopes

Vertical profiles of stable lead isotopic ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ $^{206}Pb/^{207}Pb$) in the Baie and Mer Bleue cores are shown in Fig. 2.7 and reported in Tables 2.6 and 2.7. The Baie core displays highly variable Pb isotopic ratios ($^{206}Pb/^{207}Pb$ = 1.168-1.206) between 35 and 95 cm depth with a minimum of 1.168 at 75 cm and its most radiogenic value at 55 cm ($^{206}Pb/^{207}Pb$ = 1.206). Since the mid-19th century, the four Pb isotopic ratios have shifted towards lower values until 1965 when they start increasing slightly. This shift in isotopic values can likely be explained by the start of industrial activities and will be further discussed later. The stable Pb isotopic ratios in the Mer Bleue core exhibit less variability than in the Baie core. Samples between 75 and 90 cm depth yielded the most radiogenic ratios of the core ($^{206}Pb/^{207}Pb$ = 1.213-1.216) and are thought to represent the local natural isotopic signature, as they compare well with values from pre-industrial peat samples obtained in the region (Shotyk and Krachler, 2010) and those reported for the continental crust ($^{206}Pb/^{207}Pb \sim 1.21$; Taylor and McLennan, 1995) . During the past two centuries, $^{206}Pb/^{207}Pb$ values in the Mer Bleue core display a similar pattern as in the Baie core with ratios being more radiogenic (1.178 vs 1.165).

2.4. Discussion

2.4.1 Lead concentrations and accumulation rates

The increase in Pb concentrations and accumulation rates are nearly synchronous between the three study sites (Figs. 2.4 and 2.5). This increase is observed in enrichment factors as well (Appendix 1.1). This observation implies that a common source of lead was likely deposited at the three sites during the same period. The Baie core shows a broad peak spanning from 1951AD to 1961 AD whereas the Pb accumulation rate patterns in the Mirabel and Mer Bleue cores are nearly identical with peaks in the 1940's and the late 1960's to early 1970's. Given the lower peat accumulation rate during this period in the Baie bog, the lower resolution Pb accumulation rate profile may hide a double peak similar to the other two cores.

The Pb AR peak found around the mid-1960's in the three cores is consistent with results of other studies carried out in the region. The analysis of the Point Escuminac bog in New Brunswick revealed multiple peaks in Pb accumulation rates corresponding to 1850 AD, 1960 AD and 1996 AD and ranging between 17 and 39 mg cm^{-2} yr^{-1} (Kylander *et al.*, 2009). Lead deposition rates recorded in sediments of a Canadian Shield lake in Quebec (Lac Tantaré, near Quebec City) display a single peak at around 1975 AD (Gallon *et al.*, 2005). A peak in Pb concentrations with similar timing was found in a peat core recovered at Spruce bog, 200 km north-west of the Mer Bleue bog (Shotyk and Krachler, 2010). The first Pb AR peak dated at 1940's in the Mirabel and Mer Bleue cores is not reported in other studies. Nevertheless, based on their interpretation of the Lake Tantaré sediment record, Gallon *et al.* (2005) proposed that coal burning in the U.S.A. and Canada was the main source of atmospheric Pb in the 1920's and in the late 1940's to early 1950's. Givelet *et al.* (2003) reported Pb concentration peaks dated to the late 1950's in three peat bog cores recovered in southern Ontario and also impute its source to coal burning. Results of these studies are consistent with the presence of a broad peak in accumulation rates observed in the Baie core (Fig 2.5). Coal burning could also explain the 1940's peak found in the Mer Bleue and Mirabel cores (Fig. 2.6). Most studies also document a rapid decline in Pb concentrations and/or accumulation rates since the 1970's, which can be explained by the phasing out of leaded gasolines and the implementation of other mitigation policies (Boutron, 1991; Gallon *et al.*, 2005; Shotyk and Krachler, 2010).

2.4.2 Arsenic and cadmium

Pb has been shown to be immobile in peat bogs and thus provides a truly representative historical record of its atmospheric deposition (Shotyk et al., 1998; Vile et al., 1999; Weiss et al., 1999b). Given the similarities of the As and Cd profiles with Pb (Fig. 2.4) and despite the differences in their geochemical behavior, it would appear that the As and Cd records were unaffected by post-depositional remobilization and that these bog cores can be used as reliable archives of atmospheric As and Cd deposition.

Based on the interpretation of lacustrine sedimentary records, atmospheric deposition of anthropogenic As (Lac Tantaré near Quebec City, 47°04′15″N, 71°33′42″ W) was found to start around 1850 AD and peaked during the 1950's (Couture *et al.*, 2008, 2010). The peak in As deposition was correlated to polycyclic aromatic hydrocarbon (PAH) accumulation and attributed to coal burning which peaked during the middle of the 20th century (Couture *et al.*, 2008). Likewise, our bog core records display an increase in the As accumulation rate at 1850-1900 AD (Fig. 2.5), but two AR peaks appear in the Mirabel and Mer Bleue cores at ~1940AD and 1960-1970AD. The first peak can reasonably be ascribed to coal burning as it corresponds with a peak in north-eastern North America coal consumption (Fig. 2.6) (Graney *et al.*, 1995). The second peak probably originates from coal burning as well, since coal consumption as a means of electrical power generation has steadily increased in the U.S. and Ontario since the end of the 1950s (Fig. 2.6) (Graney *et al.*, 1995). The decreasing As accumulation rate after the late 1960's can be explained by the gradual implementation of emission control policies and the proportionally faster increase in the use of "cleaner" energies like oil, nuclear fuels and hydroelectricity. Arsenic accumulation rates in the Baie core do not reflect any particular pattern, with a maximum around 180 µg m^{-2} yr^{-1} in 1915-1925. The maximum AR value obtained in this core is about a third of the maximum values observed in Lake Tantaré and Bédard Lake sediments (Couture *et al.*, 2008, 2010).

The onset of important anthropogenic Cd pollution dates back to 1850-1900 AD, depending on the site (Fig 2.4 and 2.5; Annexe 1.1). Alfaro-De la Torre and Tessier (2002) reported an increase in Cd fluxes starting around 1880AD in Lake Tantaré. Likewise, Cd concentrations and accumulation rates were found to increase around 1850 in Greenland snow and ice (Boutron *et al.*, 1995) and in three lakes from Maine and Massachusetts (450-600 km SE; Norton *et al.*, 2007).

Like Pb and As, the Cd accumulation rates in the Mer Blue and Mirabel bog cores display a “bimodal” pattern with peaks dated at ~1940AD and the mid-60’s (Fig. 2.5). The 1960’s peak is in good agreement with results from other studies in the region which documented a decrease in Cd accumulation in lake sediments after 1967AD in southern Quebec (Lac Tantaré, Alfaro-De la Torre and Tessier, 2002), in the mid-60’s in Greenland snow and ice (Boutron *et al.*, 1991; 1995) and 1965-1975 in three lake cores from the NE U.S.A. (Norton *et al.*, 2007). The peak dated at ~1940AD in the Mirabel and Mer Bleue cores was not reported in those studies, but, like for Pb and As, coal burning could explain the presence of this peak in our cores as it corresponds with an increase in coal consumption in the north-eastern North America (Fig. 2.6). Again, Cd ARs do not display any particular temporal pattern in the Baie core and rates are about one order of magnitude lower than those obtained by Alfaro-De la Torre and Tessier (2002) in Lake Tantaré.

2.4.3 Nickel and zinc

The Zn surface enrichment observed in the three cores (Fig. 2.4; Appendix 1.1) is likely explained by bioaccumulation by plants. This phenomenon has been reported in a number of other studies (Livett *et al.*, 1979; Raush *et al.*, 2005). Consequently, an historical reconstruction of atmospheric Zn deposition is more tenuous, yet the Zn concentrations at the three sites are high enough that we can confidently suggest that a significant amount of anthropogenic Zn was deposited. Notwithstanding the surface enrichment peak in the Mirabel core, other Zn peaks are nearly coincident with the Pb peaks in the Mirabel and Mer Bleue cores and likely originate from the same source. For example, the Zn peak in the Mer Bleue core occurs at ~1970AD, in good agreement with the record obtained from Greenland ice and snow (Boutron et al., 1995). Nevertheless, the Zn source is unlikely the same as in the Greenland core as a Zn peak should also have appeared in the Baie core record as well. Hence the correspondence of the Zn peak with the Greenland core record may be fortuitous.

The Ni AR and enrichment factors through time clearly shows remobilization in the Baie (Fig. 2.5, Annexe 1.1) core, as multiple peaks are present and cannot be attributed to any known local source. Ni is known to be remobilized by redox processes (Nieminen *et al.*, 2002; Ukonmaanaho *et al.*, 2004; Raush *et al.*, 2005). Nevertheless, the Ni concentrations and AR profiles in the two other cores (Fig. 2.4b, c, 2.5) are very similar to those of other metals, namely As, Cd and Pb, implying that they probably reflect the same source function.

2.4.4 Lead isotopes

It is probably fair to assume that the nearly constant Pb concentrations (Fig. 2.4), accumulation rates (Fig. 2.5), enrichment factors (Annexe 1.1) and $^{206}Pb/^{207}Pb$ values (Fig. 2.6) at the bottom of the Mer Bleue core (below 75 cm) are representative of the natural background values. The isotopic composition falls within the range of values reported for North American dust sources ($^{206}Pb/^{207}Pb$ = 1.15-1.22; Brown, 1962). The higher variability of the $^{206}Pb/^{207}Pb$ values at the bottom (beyond ~50 cm) of the Baie core (Fig. 2.7) probably reflect a mixture of North American dust and a contribution from the Canadian Shield (0.93-1.08) which is exposed close (< 10 km) to the coring site. The lower isotopic values correspond with peaks in Pb and Sc concentrations as well as with the presence of charcoal layers. These values can likely be explained by drier periods during which more continental dust from the Canadian Shield was deposited. The effect of human activities is unlikely but cannot be completely excluded as the region was inhabited by Native North Americans during the whole period covered by the core (Frenette, 1996).

Based on the stable Pb isotope profiles (Fig, 2.7) and detailed signatures (Tables 2.6, 2.7), lead pollution through industrialization is first detectable in 1810 AD in the Mer Bleue core and 1860 AD in the Baie core. This is consistent with the Pb concentration and accumulation rate profiles as they more than double at this time at both sites (Fig. 2.4, 2.5). Both dates are in good agreement with other records derived from peat bogs and lake sediments collected in eastern North America. The onset of significant anthropogenic contamination was reported as 1850-1870 AD in southern Quebec (Gallon *et la.*, 2005, 2006), 1885 AD in New Brunswick (Kylander *et al.*, 2009), 1800 AD in eastern Ontario (Shotyk and Krachler, 2010), 1800 AD and 1880 AD in the Hudson Bay region (Outridge *et al.*, 2002) and 1860 AD in the Great Lakes region (Graney *et al.*, 1995). Higher isotopic ratios are observed around 1860 AD and 1810 AD in the Baie and Mer Bleue cores, respectively. Similar peaks during the mid-1800's were reported by Gallon *et al.* (2006) in several Quebec lakes and linked to smelting of Pb ores from the Upper Mississippi Valley. It was recently suggested that the peak reported by Gallon *et al.* (2006) could be used as a chronological marker (Tessier *et al.*, 2012). The peak in the Baie core (1860AD) may correspond to this marker, whereas the peak in the Mer Bleue core (1810AD) is older (Fig 2.7). The mid-1800's peak was not observed by Shotyk and Krachler (2010) in the Spruce bog of Ontario.

The impact of leaded gasoline emissions on the $^{206}Pb/^{207}Pb$ values is visible since the 1940's in both our cores (Fig. 2.7), with values remaining relatively constant until the 1970's. This period corresponds with the period of maximum Pb concentrations and accumulation rates (Fig. 2.4 and 2.5). The $^{206}Pb/^{207}Pb$ increases after leaded gasolines were gradually phased-out (1976AD), but does not return to historical background values. Shotyk and Krachler (2010) obtained a similar record in central Ontario and attributed it to the proportionally growing importance of other industrial processes, such as metal smelting and refining (specifically the Noranda smelter), which release less radiogenic Pb to the atmosphere. The Noranda smelter is the most important atmospheric Pb point source in Canada (Sturges and Barrie, 1989). Blais (1996) pointed out that Ni and Cu ore smelting and refining were an especially important source of atmospheric Pb in Quebec. Furthermore, Sturges and Barrie (1989) attributed the less radiogenic Pb signatures measured in aerosols from Dorset in 1984 and 1986 ($^{206}Pb/^{207}Pb$ = 1.12 and 1.10 respectively) to emissions from the Noranda smelter.

To determine the relative contribution of various sources of atmospheric Pb deposition in the Baie and Mer Bleue cores, all samples and relevant end-members were plotted as $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{204}Pb$ in Fig. 2.8. Many of the potential Pb sources, including natural sources, fall within a similar range of values. In both cores, isotope ratios are shifted towards less radiogenic values

($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{204}Pb$) with a "transition" predating the introduction of leaded gasoline. Based on the analysis of Lake Erie sediments, coal burning was found to be the most important source of Pb between 1850-1920 AD (Graney *et al.*, 1995). Furthermore, smelting activities likely contribute to the less radiogenic compositions as two important smelters (Noranda and Sudbury) were started up at the beginning of the 20th century. The clusters of data at the bottom left of the figure for each core represent the shift from coal burning and smelting activities to leaded gasoline emissions, with the samples from the Baie core plotting closer to the Canadian aerosol values than those from the Mer Bleue core. As mentioned previously, the persistent low isotopic ratios in both cores can be explained by the growing importance of industrial Pb sources relative to Pb from leaded gasolines since their phasing-out.

Apportionment of various sources of Pb was made using the following $^{206}Pb/^{207}Pb$ end-member values: 1.215 and 1.186 for natural background in the Mer Bleue and Baie cores respectively, 1.151 and 1.217 for atmospheric Pb (dominated by leaded gasoline emissions) from eastern Canada and the eastern and Midwest U.S.A., respectively, based on a range of published ratios (Rabinowitz and Wetherill, 1972; Sturges and Barrie, 1987, 1989; Gallon *et al.*, 2005). The relative contribution of each of these sources was calculated using a simple linear mixing equation:

$$F_1 + F_2 + F_3 = 1 \tag{5}$$

$$R_1^i F_1 + R_2^i F_2 + R_3^i F_3 = R_{measured}^i \tag{6}$$

where R^i are the $^{206}Pb/^{207}Pb$ ratios, and F_1, F_2, F_3 are the fraction of the three end-member Pb sources. From the 1960's, Mississippi Valley sulfide ores (Missouri, Iowa) were the main source of Pb in gasoline additives in the U.S. with minor contributions from Mexican and Peruvian ores (Sturges and Barrie, 1987; Rosman et al. 1994), whereas the Bathurst (New Brunswick) volcanic-sediment hosted massive sulfide (VSHMS) (Goodfellow, 2002) deposits were as the source of lead for the additive in Canadian gasolines (Sturges and Barrie, 1987). The variability of the isotopic ratios for the period following the phase out of leaded gasolines in the 1980's renders the quantification of U.S.A. and Canada Pb deposition more difficult because of the decrease in its atmospheric Pb contribution relative to other emergent industrial sources (Böllhofer and Rosman, 2002) as well as the use of a greater variety of Pb sources, including recycled Pb. Therefore, no attempt to calculate the relative contributions of Pb sources was made beyond 1980. The estimated, relative proportions of the various sources, for the period (1960 to 1976) during which leaded gasoline was the dominant source, of Pb to the atmosphere, reveal that 55% and 35% of the anthropogenic lead in the Mer Bleue and Baie cores respectively, originated from U.S. aerosols. Comparatively, Sturges and Barrie (1987) estimated that between 24% and 43% of the atmospheric Pb measured in atmospheric aerosols sampled in Dorset (Ontario) in 1984 and 1986 was coming from the U.S.A., whereas Carignan and Gariépy (1995) reported U.S. contributions of atmospheric Pb to be approximately 60% in epiphytic lichens collected in the St. Lawrence Valley (Montreal to Saguenay) between 1990 and 1994. The apportionment calculations show that more atmospheric Pb from the U.S.A. was deposited in the Mer Bleue core than in the Baie core between 1960 and 1976. A similar decreasing contribution from U.S. aerosols away from the U.S. north-east along the St. Lawrence Valley was reported in other studies (Carignan and Gariépy, 1995; Carignan *et al.*, 2002; Lucotte *et al.*, 1995; Simonetti *et al.*, 2000).

2.4.5 Comparison of the trace metal records

Our three atmospheric trace metal deposition and lead isotope records were compared among themselves to determine if metals originated from a common source. The increases in the AR of As, Cd, Pb and, to a certain extent, Ni are reasonably coincident in the Mirabel and Mer Bleue cores (Fig. 2.5). The trace metal AR peaks recorded at ~1940AD may reflect input from coal burning and smelting activities as they constitute important sources of the targeted metals (Nriagu and Pacyna, 1988). As mentioned previously, based on PAH profiles, Gallon *et al.* (2005) attributed the Pb emissions in the first half of the 20th century to coal burning. At the same site and over the same period, coal burning was identified as the predominant source of As (Couture *et al.*, 2008). Hence, the presence of this As AR peak may be explained by the greater time resolution of the peat cores in comparison to lacustrine sediments. The date corresponds roughly with World War II and could reflect an increase in industrial activity in support of it. This event, however, is not recorded in the $^{206}Pb/^{207}Pb$ (Fig. 2.6) profile of the Mer Bleue or Baie cores, nor is a trace metal peak observed in the Baie core at that time, which suggest that the lower resolution of the Baie core data cannot reveal this event. The Pb AR peak extending between 1951 and 1961 in the Baie core, likely originates from the same source as in the two other cores i.e. coal-burning, since the timing of the peak (Fig 2.6) corresponds with a peak in coal consumption (Graney *et al.*, 1995). Alternatively, the source of Pb that contributes to the peak may be local since industrial development (aluminum smelter, port, pulp and paper industry, etc.) in the city of Baie-Comeau roughly started at that time (Frenette, 1996).

Identifying a precise source for the targeted metals in our study area is difficult given the great number of industries in the Great Lakes and St. Lawrence Valley region. They most likely originate from a variety of trace metal emissions. The discrepancies between sites, mainly between the Baie and the two other cores (Mirabel and Mer Bleue cores), could be ascribed to the accuracy of the age-depth models or distance from sources (discussed in the next paragraph). Diagenetic remobilization cannot be completely ruled out as the trace metal profiles in the Mirabel and Mer Bleue cores are similar to those of Fe, a metal that is readily affected by redox processes. On the other hand, Mn, which is typically more redox sensitive than Fe, does not display similar profiles. Differential hydrological or geochemical conditions can also be invoked to explain the Baie core particularities. Elucidation of the discrepancies would require an analysis of the pore-water metal concentrations but this was beyond the scope of the study.

The higher metal AR in Mirabel and Mer Bleue cores can be explained by their proximity to urban centers, the more industrialized areas of the St. Lawrence and Ottawa Valleys, and the U.S. Mid-West and Great Lakes region. According to our estimates of source apportionment of stable Pb isotopes (section 2.2.4), U.S. aerosols accounted for 55% of the atmospheric Pb deposition in the southwest while it still accounted for 35% of the deposition in the northeast, at least for the main period of leaded gasoline consumption (1960-1976 AD). These observations highlight the importance of cross-border transport of Pb, and likely other metals, from the U.S. Mid-West to the Canadian east coast. The decrease in atmospheric metal deposition rates starting in the early 1970's, as revealed by the sharp decrease in trace metal concentrations (Fig. 2.4) and accumulation rates (Fig. 2.5) in the three cores, reflects the efficiency of the implementation of various government regulations and mitigation policies during this period (phasing-out of leaded gasolines (1976), Clean Air Act (1970), etc.). To summarize, the three bog cores have recorded the main trends in atmospheric trace metal deposition and emissions for the eastern part of the North American continent, i.e., the burning of coal for electricity production, metal ore smelting and refining, as well as the rise and fall in leaded gasoline consumption. Nevertheless, as may be the case of the Baie core, these records may have been "overprinted" by a local signal.

2.5 Conclusion

The history of trace metal deposition was reconstructed using cores from three different peat bogs along the St. Lawrence Valley (SLV). Based on the metal concentration profiles and ^{210}Pb and ^{14}C chronologies, metal accumulation rates were estimated over the period recorded by the cores. These data and the Pb isotopic composition were used to mark the impact of the onset of the Industrial Revolution at 1810-1850 AD in the SLV. For some metals (Zn and Ni), historical reconstruction was more tenuous due to bioaccumulation or post-depositional remobilization processes. Coal-burning and metal-ore smelting and refining are believed to be the main sources of trace metal pollution between 1850-1920AD and, at least for Pb, to the use of leaded gasolines starting in 1923 until their phasing-out in 1976AD. Results show that the two cores recovered at the southwestern end of the St. Lawrence Valley (Mer Bleue and Mirabel peatlands) have a much higher trace metal content than the Baie core, as expected given their proximity to large urban and industrial centers of the St. Lawrence and Ottawa Valleys and U.S. Mid-West. Hence, the three cores recorded mainly the metal deposition from regional sources (U.S. Mid-West, St. Lawrence and Ottawa Valleys) brought by long-range transport (>1000 km) of contaminants, with potentially some weaker local (<50 km) signals. Although the metal accumulation rates are still an order of magnitude higher than the pre-industrial levels, a significant decrease in deposition rates since the mid-1960's shows that mitigation policies have been effective in reducing trace metal emissions to the atmosphere.

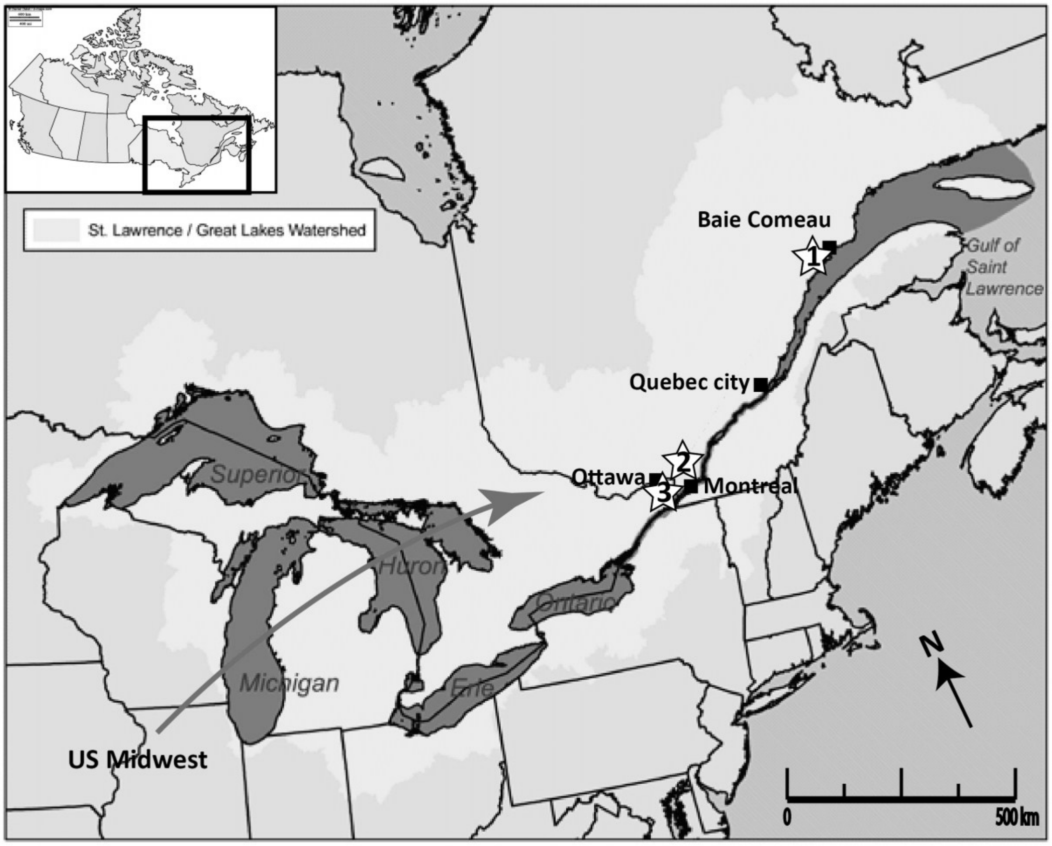


Figure 2.1: Location of study sites 1. Baie bog, 2. Mirabel bog, and 3. Mer Bleue bog. The grey arrow represents the general direction of the prevailing winds.

Table 2.1: Mean statistics calculated from the analyzed standards (see text).

	As	Ca	Cd	Fe	Mn	Ni	Pb	Sc	Sr	Zn
Mean DL	0.03	6	0.03	10	1.5	0.2	0.03	0.06	0.3	0.4
Mean error	5.9	4.4	14	12	3.3	2.1	1.6	17	6.6	4.4
Mean reproducibility	67	97	83	95	94	90	86	83	97	92

Mean DL: mean detection limit (3σ), reported in ppb. Mean error (%, n=9) = [(mean standards values - certified values)/certified values]*100. Mean reproducibility (%, n=9) = [(mean standard values – standard deviation)/mean standard values]*100.

Table 2.2: Results of ^{210}Pb analyses for the Baie core

Depth (cm)	^{210}Pb date (AD)	Uncertainty (yr)	Depth (cm)	^{210}Pb date (AD)	Uncertainty (yr)
0-1	2009	0.05	18-19	1971	1.8
2-3	2007	0.2	20-21	1963	2
4-5	2002	0.3	22-23	1951	2.5
6-7	1997	0.5	24-25	1941	3
8-9	1992	0.7	26-27	1931	3.6
10-11	1988	0.8	28-29	1905	5.1
12-13	1984	1.1	30-31	1878	6.8
14-15	1981	1.1	32-33	1862	5.9
16-17	1975	1.5	34-35	1845	7.1

Table 2.3: Results of ^{210}Pb analyses for the Mirabel core

Depth (cm)	^{210}Pb date (AD)	Uncertainty (yr)	Depth (cm)	^{210}Pb date (AD)	Uncertainty (yr)
0-1	2009	0.05	20-21	1972	1.4
2-3	2007	0.1	23-24	1968	1.4
4-5	2004	0.2	26-27	1964	1.5
6-7	2001	0.3	28-29	1960	1.9
8-9	1999	0.4	31-32	1955	2.2
10-11	1994	0.6	33-34	1950	2.3
12-13	1988	0.8	36-37	1939	3
14-15	1984	0.9	39-40	1927	2.8
16-17	1980	1.1	41-42	1909	4.3
18-19	1976	1.3	43-44	1856	5.5

Table 2.4: Results of ^{210}Pb analyses for the Mer Bleue core

Depth (cm)	^{210}Pb date (AD)	Uncertainty (yr)	Depth (cm)	^{210}Pb date (AD)	Uncertainty (yr)
1-2	2010	0.06	24-25	1989	0.8
3-4	2008	0.1	26-27	1986	0.9
5-6	2007	0.2	28-29	1984	1.0
7-8	2005	0.2	30-31	1981	1.1
9-10	2003	0.3	32-33	1975	1.3
11-12	2001	0.4	34-35	1969	1.6
13-14	1999	0.5	36-37	1964	1.8
15-16	1998	0.5	38-39	1958	2.0
17-18	1997	0.5	40-41	1949	2.7
18-19	1995	0.6	42-43	1916	4.0
20-21	1993	0.7	44-45	1886	6.2
22-23	1991	0.8	46-47	1799	10.6

Table 2.5: Results of ^{14}C AMS measurements, calibrations and description of samples

Site	Depth (cm)	Laboratory number	^{14}C age (BP)	2σ range (cal yr AD)	Material dated
Baie	32-33	UCIAMS-102304	70±20	1696-1918	*Sphagnum* spp. stems
	46-47	UCIAMS-107370	170±15	1667-1950	*Sphagnum* spp. stems, branches and leaves
	59-60	UCIAMS-107371	305±15	1520-1644	*Sphagnum* spp. stems
	72-73	UCIAMS-102305	455±20	1423-1453	Charcoals, charred *Picea* needles
	96-97	UCIAMS-102306	1065±20	898-1019	*Sphagnum* spp. stems
Mer Bleue	46-47	UCIAMS-102301	135±20	1674-1957	Charcoals, charred *Picea* needles, Ericacea leaves
	56-57	UCIAMS-107372	-600±15*		*Sphagnum* spp. stems, branches and leaves
	63-64	UCIAMS-107373	235±15	1646-1798	*Sphagnum* spp. stems
	72-73	UCIAMS-102302	865±25	1049-1250	*Sphagnum* spp. stems
	89-90	UCIAMS-102303	1445±20	579-648	*Sphagnum* spp. stems
Mirabel	44-45	UCIAMS-102307	165±20	1666-1953	Charcoals, charred *Picea* needles
	48-49	UCIAMS-107374	140±20	1671-1942	*Sphagnum* spp. stems

*date rejected: contains excess ^{14}C, probably from sample contamination.

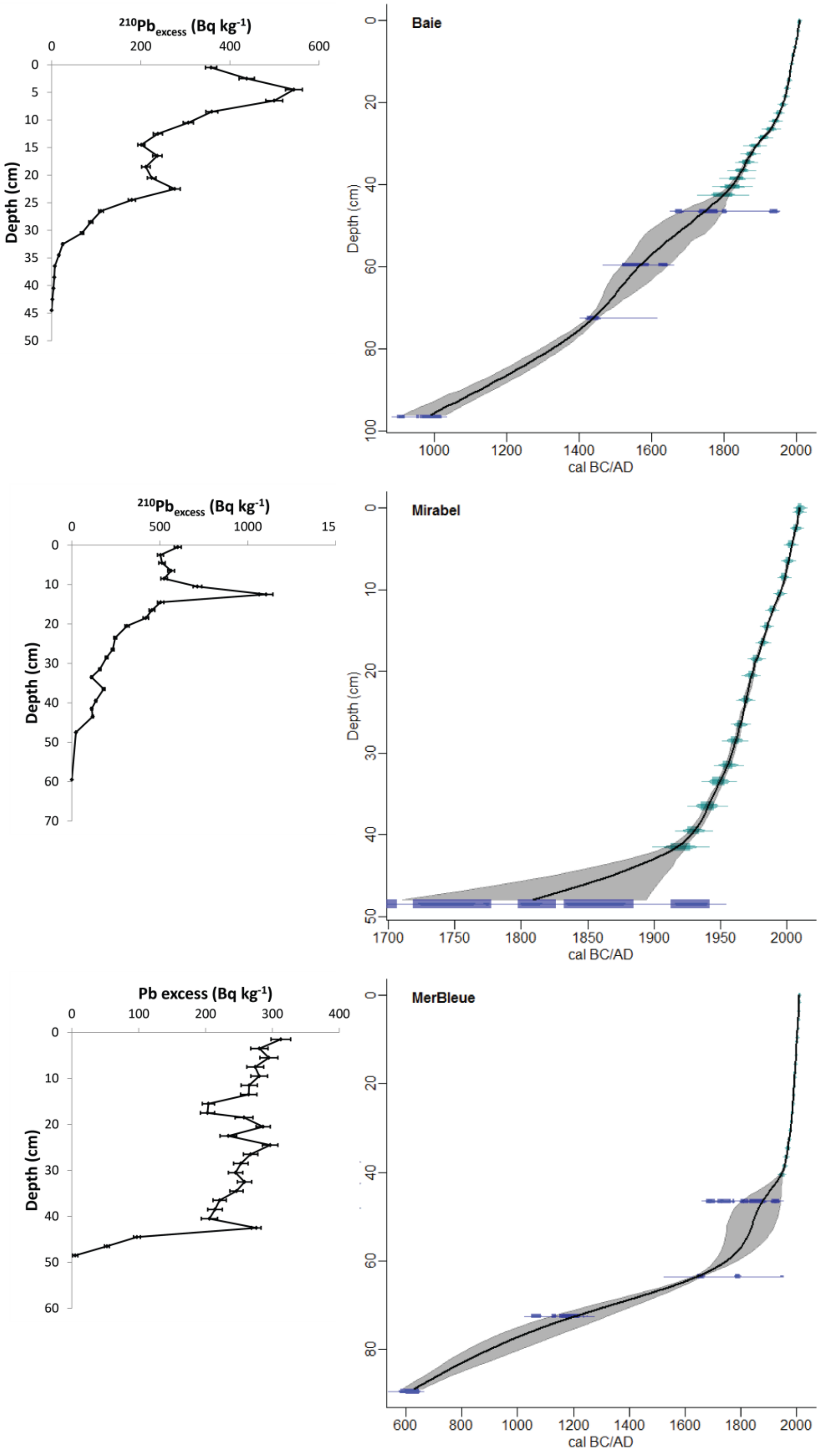


Figure 2.2: Excess ^{210}Pb (black diamonds) activities vs. depth for the three cores and age-depth models including ^{210}Pb and ^{14}C dates for the Baie, Mirabel and Mer Bleue cores. The grey area represents the 95% confidence interval. Note that age-depth models do not cover the same depth ranges nor the same periods.

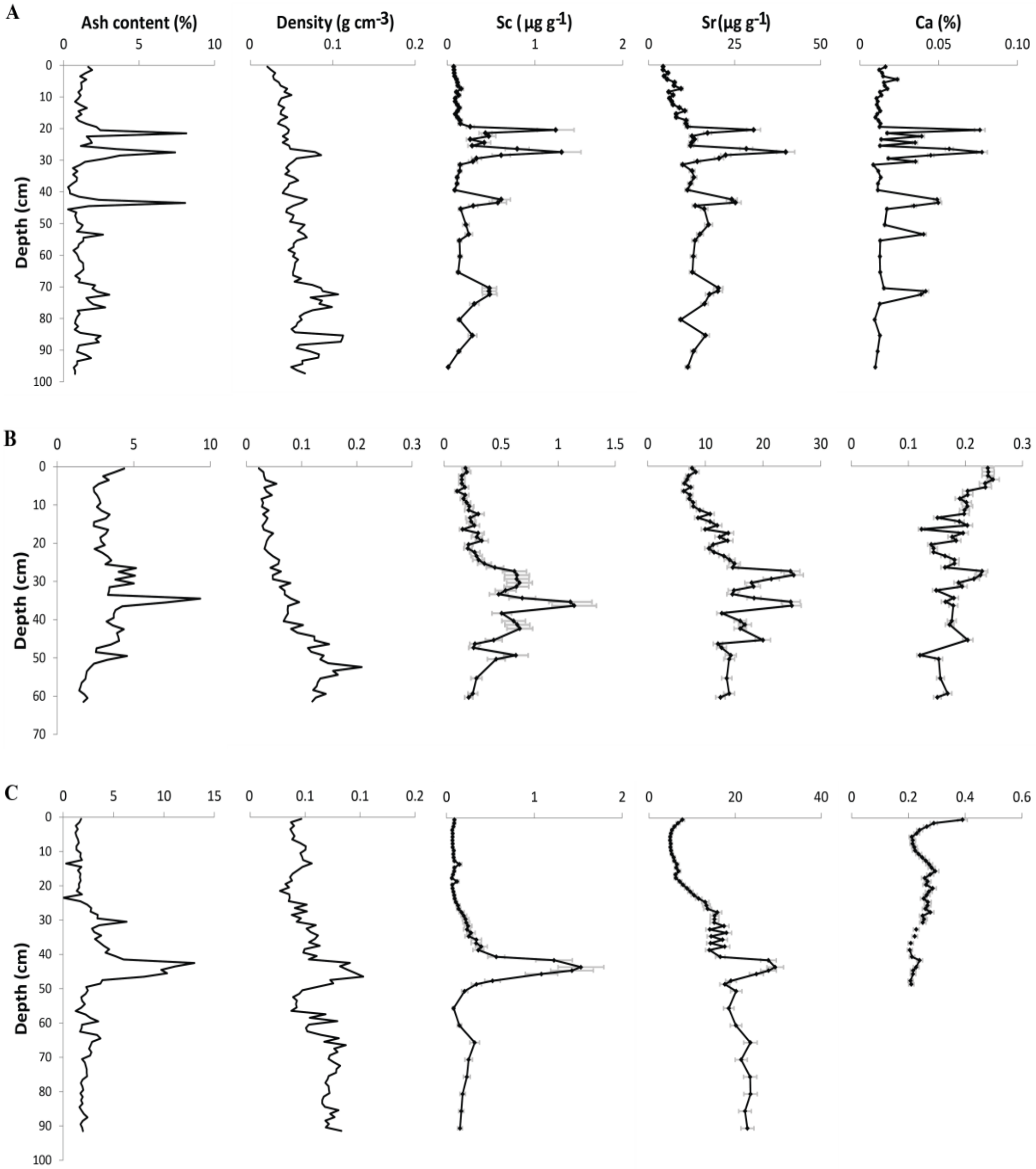


Figure 2.3: Vertical profiles of ash content, bulk density and Sc, Sr and Ca concentrations in cores recovered from the Baie (A), Mirabel (B) and Mer Bleue (C) bogs. Ca concentrations for the second half of the Mer Bleue core as they were deemed as unreliable.

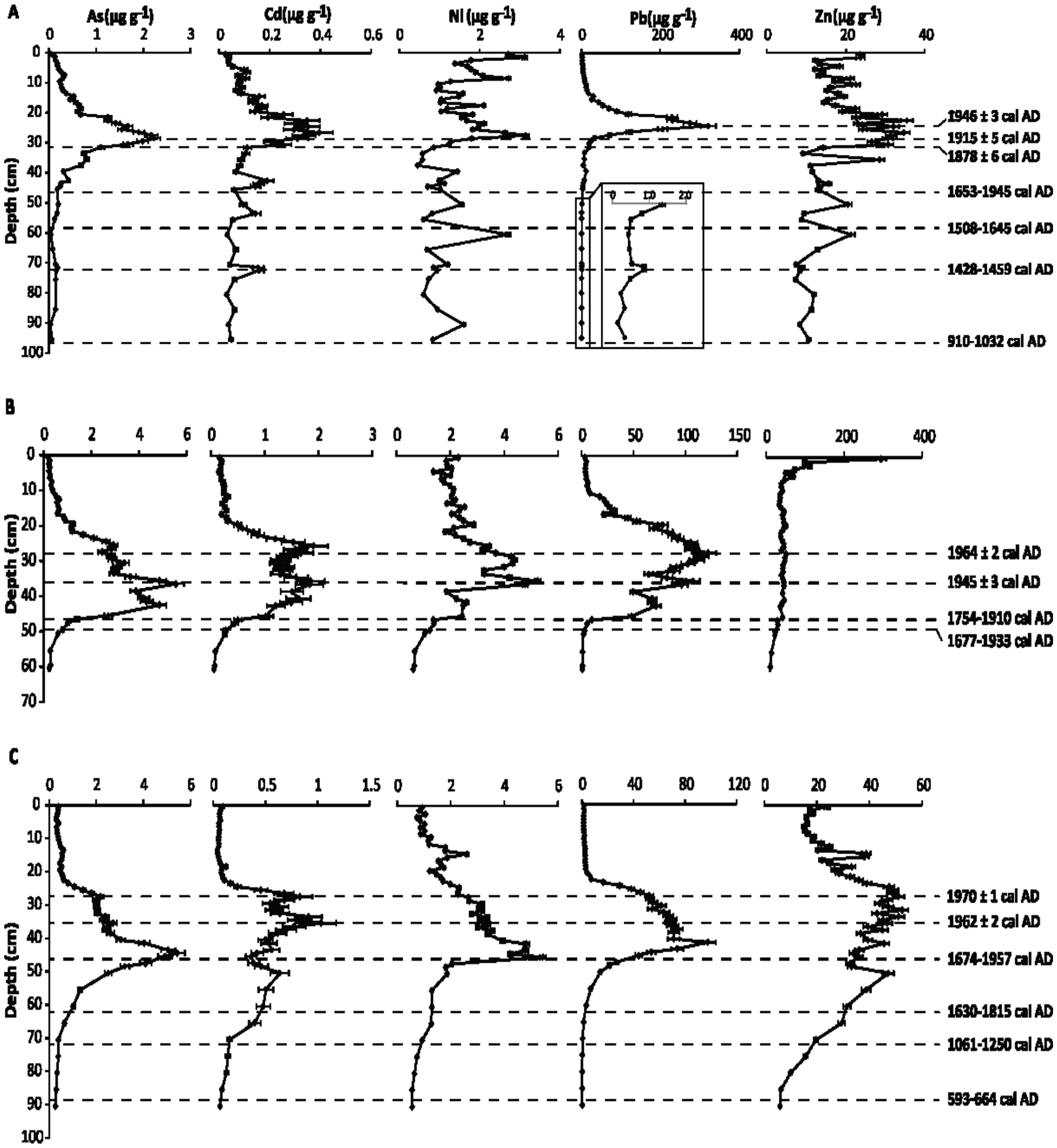


Figure 2.4: Vertical profiles of Pb, As, Cd, Ni and Zn concentrations in the cores recovered from the Baie (A), Mirabel (B) and Mer Bleue (C) bogs. The age dates correspond to ^{210}Pb and ^{14}C AMS dates.

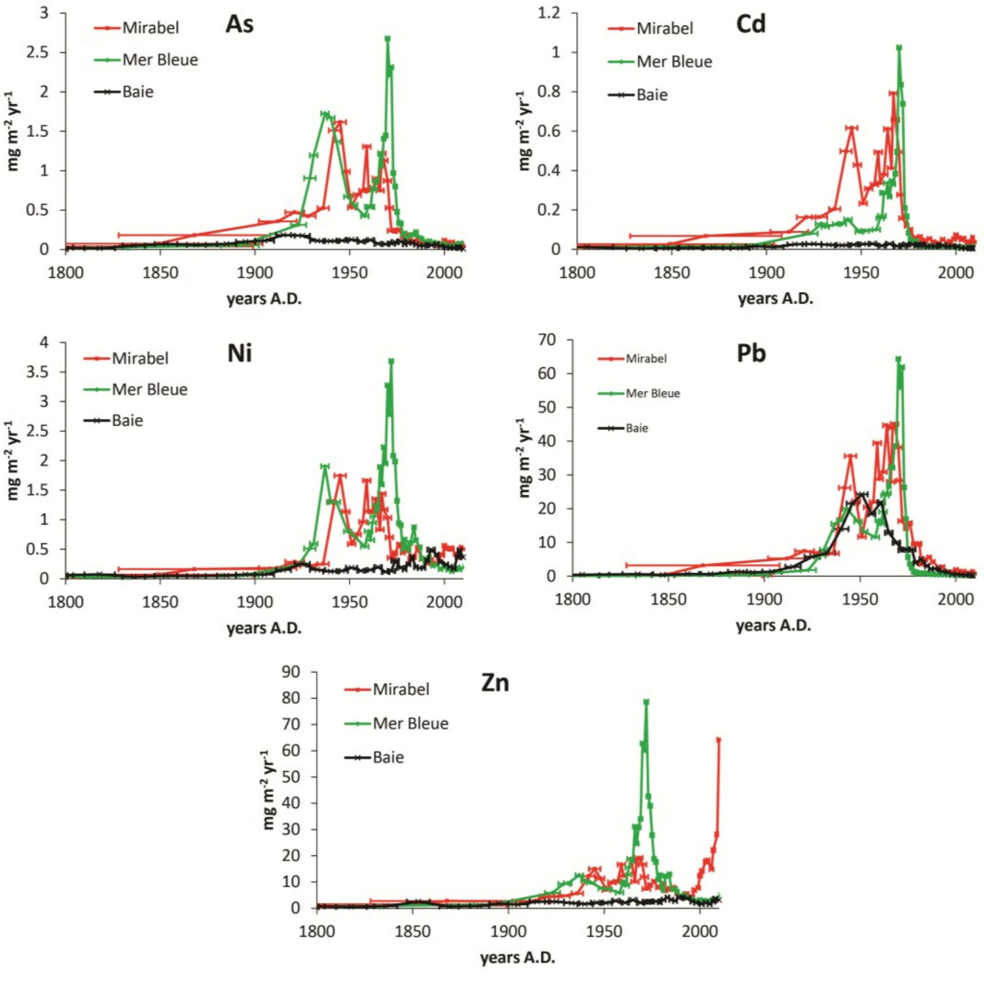


Figure 2.5: As, Cd, Ni, Pb and Zn accumulation rates in the Mirabel (red), Baie (black), and Mer Bleue (green) cores. Note that As and Cd accumulation rates are in µg m^{-2} yr^{-1} while those of Ni, Pb and Zn are in mg m^{-2} yr^{-1}.

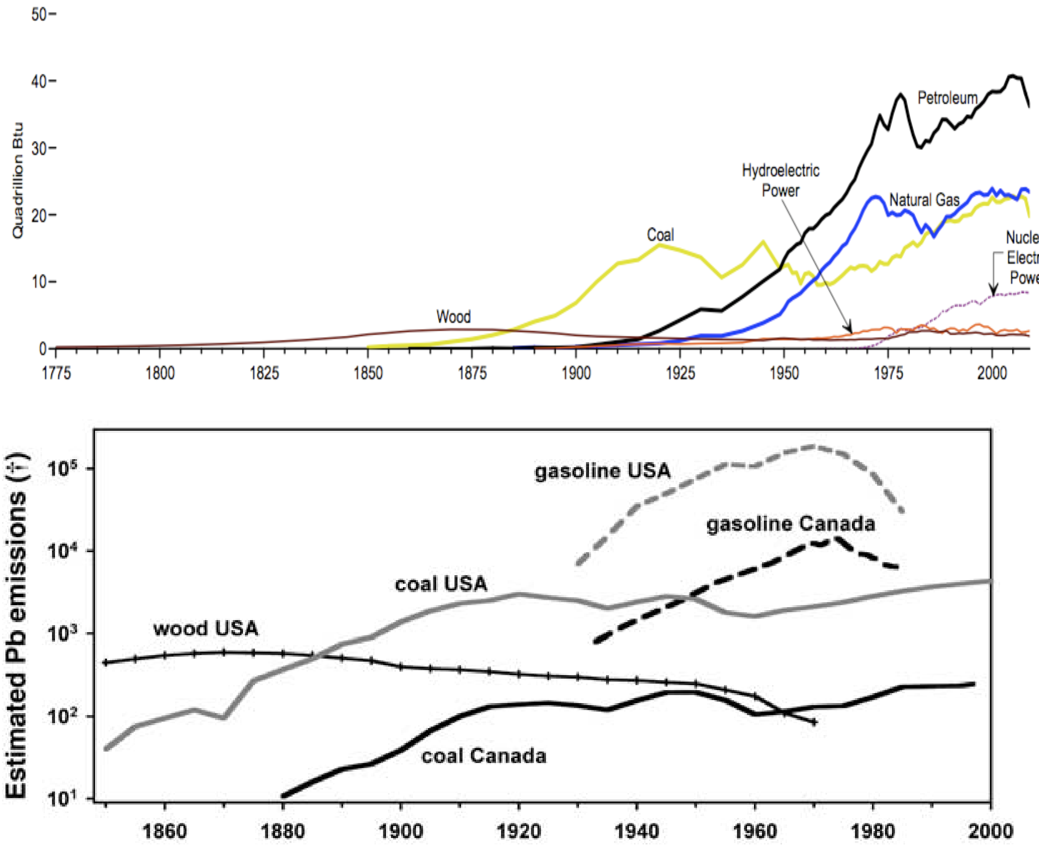


Figure 2,6: Top figure: U.S. primary energy consumption by source 1775-2009 (U.S. EIA, 2010). Bottom figure: U.S. and Canada estimated Pb emissions from wood, coal and gasoline combustion (Gallon *et al.*, 2005).

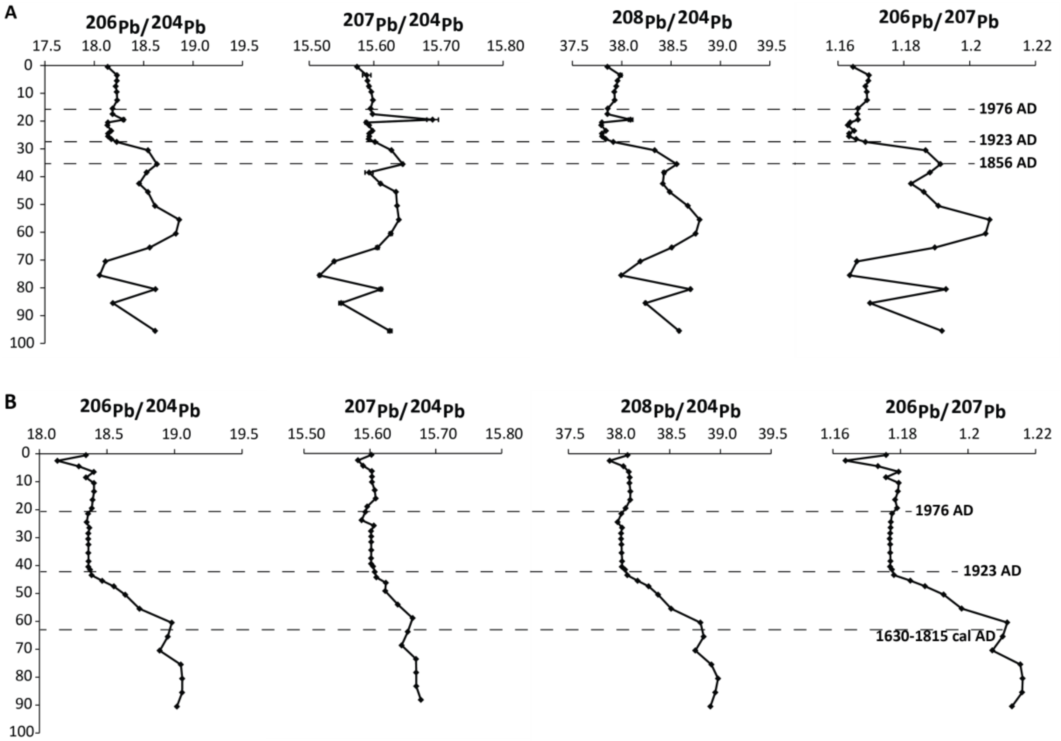


Figure 2.7: Vertical profiles of ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb and ^{206}Pb/^{207}Pb in the Baie (A) and Mer Bleue (B) bog cores. Dates represent the date of a potential chronological marker present in several lakes of Quebec (Gallon *et al.*, 2006), the introduction of leaded gasolines (1923) and their initial phasing out (1976).

Table 2.6: $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ isotopic ratios in the Baie core.

Depth (cm)	$^{208}Pb/^{204}Pb$	2se	$^{207}Pb/^{204}Pb$	2se	$^{206}Pb/^{204}Pb$	2se	$^{208}Pb/^{206}Pb$	2se	$^{207}Pb/^{206}Pb$	2se
0.5	37.8559	0.0013	15.574	0.0004	18.1367	0.0005	2.0872	0.00003	0.8587	0.00001
3.5	37.9866	0.016	15.5889	0.0065	18.2303	0.0073	2.0838	0.00006	0.8551	0.00003
5.5	37.9575	0.001	15.5901	0.0003	18.2283	0.0003	2.0823	0.00003	0.8553	0.00001
7.5	37.9458	0.0036	15.5924	0.0015	18.2175	0.0017	2.0829	0.00004	0.8559	0.00001
9.5	37.9257	0.0007	15.5961	0.0003	18.2279	0.0002	2.0806	0.00002	0.8556	0.00001
12.5	37.9295	0.0014	15.5986	0.0005	18.2322	0.0005	2.0803	0.00004	0.8555	0.00001
15.5	37.8587	0.0032	15.595	0.0011	18.1854	0.0008	2.0819	0.00008	0.8576	0.00002
17.5	37.8559	0.0011	15.598	0.0003	18.1863	0.0003	2.0817	0.00002	0.8577	0.00001
19.5	38.0899	0.0225	15.691	0.009	18.2967	0.0106	2.0819	0.00006	0.8576	0.00003
20.5	37.7994	0.0044	15.5882	0.0018	18.1387	0.0021	2.0838	0.00004	0.8593	0.00001
21.5	37.7939	0.0016	15.5926	0.0006	18.1341	0.0006	2.0841	0.00003	0.8598	0.00001
23.5	37.84	0.0022	15.598	0.0008	18.1713	0.0012	2.0825	0.00002	0.8584	0.00001
24.5	37.8002	0.0013	15.5929	0.0005	18.1408	0.0005	2.0837	0.00002	0.8595	0.00001
25.5	37.8017	0.001	15.593	0.0004	18.1406	0.0003	2.0838	0.00003	0.8596	0.00001
26.5	37.8372	0.0008	15.5921	0.0003	18.173	0.0003	2.082	0.00002	0.858	0.00001
27.5	37.9145	0.0021	15.6018	0.0009	18.2282	0.0009	2.0801	0.00003	0.8559	0.00001
30.5	38.3346	0.0016	15.6273	0.0006	18.5438	0.0007	2.0673	0.00002	0.8427	0.00001
35.5	38.5574	0.0025	15.6448	0.001	18.635	0.0012	2.0691	0.00003	0.8395	0.00001
38.5	38.4289	0.0134	15.5926	0.0062	18.5296	0.0063	2.0745	0.00006	0.8418	0.00002
42.5	38.4164	0.0034	15.6103	0.0013	18.4543	0.0016	2.0817	0.00003	0.8459	0.00001
45.5	38.4858	0.002	15.6343	0.0008	18.5435	0.0008	2.0754	0.00002	0.8431	0.00001
50.5	38.6697	0.0021	15.636	0.0007	18.6144	0.0007	2.0773	0.00005	0.84	0.00001
55.5	38.7892	0.0013	15.6387	0.0004	18.8612	0.0004	2.0566	0.00003	0.8291	0.00001
60.5	38.7484	0.0059	15.6261	0.0024	18.8262	0.0026	2.0583	0.00004	0.83	0.00002
65.5	38.5059	0.0059	15.6056	0.0024	18.5621	0.0033	2.0745	0.00004	0.8407	0.00001
70.5	38.1886	0.004	15.5386	0.0016	18.1143	0.0018	2.1082	0.00004	0.8578	0.00001
75.5	37.9943	0.0044	15.516	0.0018	18.0542	0.0021	2.1045	0.00003	0.8594	0.00001
80.5	38.6961	0.0066	15.6108	0.0025	18.6204	0.003	2.0784	0.00004	0.8384	0.00001
85.5	38.2406	0.0085	15.5493	0.0034	18.189	0.0039	2.1024	0.00005	0.8549	0.00002
95.5	38.5811	0.0073	15.6248	0.0031	18.6169	0.0034	2.0723	0.00004	0.8392	0.00002
457.5	38.9087	0.0196	15.4683	0.0078	18.1037	0.0088	2.1493	0.00008	0.8544	0.00003
475.5	37.957	0.0036	15.3821	0.0014	17.4878	0.0016	2.1704	0.00008	0.8796	0.00002

Table 2.7: ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb, ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb isotopic ratios in the Mer Bleue core.

Depth (cm)	^{208}Pb/^{204}Pb	2se	^{207}Pb/^{204}Pb	2se	^{206}Pb/^{204}Pb	2se	^{208}Pb/^{206}Pb	2se	^{207}Pb/^{206}Pb	2se
0.5	38.0851	0.0009	15.6024	0.0003	18.3448	0.0004	2.0761	0.00002	0.8505	0.00001
2.5	37.9078	0.0024	15.582	0.001	18.1339	0.0012	2.0904	0.00003	0.8593	0.00001
4.5	38.0439	0.0033	15.5896	0.0015	18.2922	0.0016	2.0797	0.00005	0.8523	0.00002
6.5	38.0966	0.0014	15.603	0.0006	18.403	0.0006	2.0701	0.00003	0.8478	0.00001
8.5	38.1053	0.0017	15.6033	0.0007	18.3449	0.0008	2.0771	0.00003	0.8506	0.00001
10.5	38.1027	0.002	15.6031	0.0009	18.4041	0.0009	2.0703	0.00002	0.8478	0.00001
13.5	38.1123	0.0024	15.6074	0.0012	18.4049	0.0013	2.0707	0.00003	0.848	0.00001
16.5	38.1099	0.0017	15.6089	0.0007	18.3943	0.0006	2.0718	0.00003	0.8486	0.00001
19.5	38.065	0.0062	15.596	0.0021	18.3881	0.0028	2.0702	0.00005	0.8482	0.00002
21.5	38.0234	0.0034	15.5931	0.0014	18.3607	0.0016	2.0709	0.00004	0.8492	0.00002
24.5	37.9857	0.005	15.5874	0.0016	18.3501	0.0022	2.07	0.00006	0.8495	0.00002
26.5	38.0297	0.002	15.6061	0.0007	18.3704	0.0007	2.0702	0.00004	0.8495	0.00001
28.5	38.0203	0.0018	15.6017	0.0007	18.3629	0.0009	2.0705	0.00004	0.8496	0.00001
30.5	38.0205	0.0018	15.602	0.0007	18.3612	0.0008	2.0707	0.00004	0.8497	0.00002
32.5	38.0242	0.0013	15.602	0.0004	18.3634	0.0004	2.0707	0.00004	0.8496	0.00001
35.5	38.0255	0.0012	15.6021	0.0004	18.3627	0.0005	2.0708	0.00004	0.8496	0.00001
38.5	38.0309	0.0013	15.6019	0.0004	18.3643	0.0003	2.0709	0.00004	0.8496	0.00001
40.5	38.028	0.0015	15.6019	0.0006	18.3627	0.0006	2.071	0.00004	0.8497	0.00001
41.5	38.06	0.0017	15.605	0.0006	18.3755	0.0007	2.0713	0.00004	0.8493	0.00001
43.5	38.0818	0.0028	15.6074	0.0009	18.3869	0.0009	2.0711	0.00004	0.8488	0.00001
45.5	38.1838	0.0023	15.6099	0.0007	18.4654	0.0006	2.0678	0.00004	0.8454	0.00001
47.5	38.2922	0.0026	15.6242	0.0011	18.5511	0.0012	2.0642	0.00003	0.8423	0.00001
50.5	38.3863	0.0085	15.6233	0.0034	18.636	0.0045	2.0598	0.00004	0.8384	0.00001
55.5	38.5142	0.0023	15.6424	0.0009	18.7408	0.0009	2.055	0.00003	0.8346	0.00001
60.5	38.8035	0.0017	15.6649	0.0007	18.9799	0.0007	2.0445	0.00003	0.8253	0.00001
65.5	38.8355	0.0024	15.6575	0.001	18.9504	0.0012	2.0494	0.00003	0.8263	0.00001
70.5	38.7526	0.0036	15.6482	0.0014	18.8907	0.0017	2.0514	0.00002	0.8283	0.00001
75.5	38.9112	0.0025	15.6701	0.0013	19.0469	0.0016	2.0429	0.00003	0.8227	0.00001
80.5	38.9765	0.0039	15.6703	0.0016	19.0573	0.002	2.0451	0.00004	0.8222	0.00001
85.5	38.9499	0.0033	15.6704	0.0013	19.0562	0.0015	2.044	0.00003	0.8223	0.00001
90.5	38.9012	0.0046	15.6774	0.0019	19.0178	0.0023	2.0456	0.00003	0.8244	0.00001
338.5	39.2976	0.0018	15.6659	0.0006	19.2963	0.0008	2.0365	0.00003	0.8118	0.00001
348.5	38.3454	0.0015	15.5508	0.0005	18.5397	0.0006	2.0683	0.00003	0.8388	0.00001

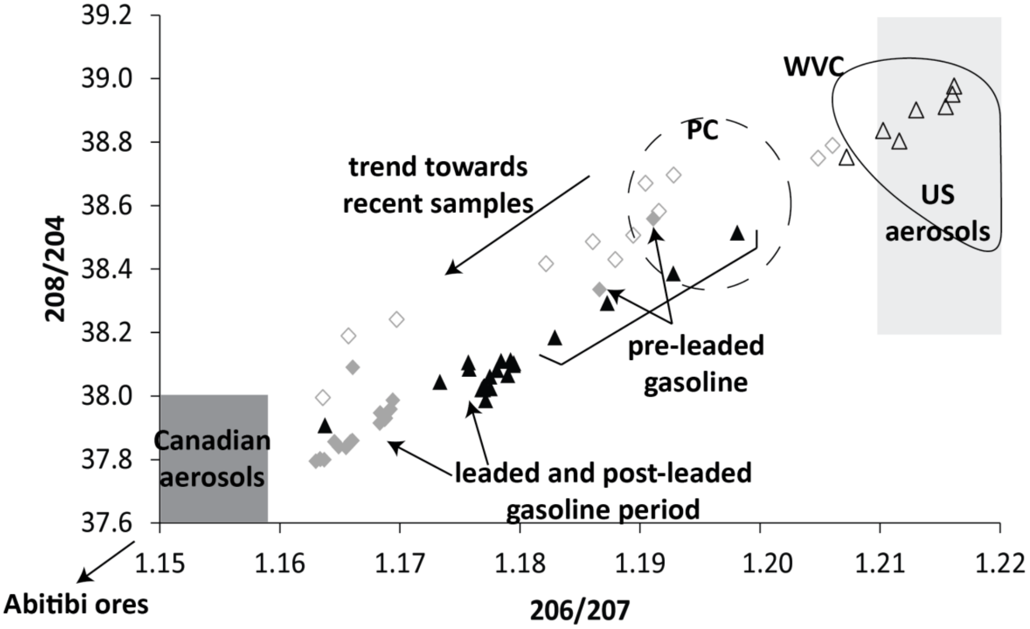


Figure 2.8: Three-isotope plot of ^{206}Pb/^{207}Pb vs.^{208}Pb/^{204}Pb. Full symbols correspond to anthropogenically-contaminated samples while open symbols represent natural signatures: grey diamonds from the Baie core, and black triangles from the Mer Bleue core. Values for Canadian and U.S. aerosols are from Graney *et al.* (1995), Abitibi ores from Simonetti *et al.* (2004). PC and WVC correspond to Pennsylvania and West Virginia coal respectively (Chow and Earl, 1972). Pre-leaded gasoline values represent samples from anthropogenic sources other than leaded gasoline, likely coal burning (1800-1920 AD) and metal-ore smelting and refining activities (1900 AD on).

2.6 References

Alfaro-De la Torre, M., and Tessier, A., 2002. Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake. *Geochim. Cosmochim. Acta,* 66, 3549-3562.

Appleby, P.G., and Oldfield, F., 1978. The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena*, 5, 1–8.

Benoit, J.M., Fitzgerald, W.F., and Damman, A.W.H., 1998. The biogeochemistry of an ombrotrophic bog: Evaluation of use as an archive of atmospheric mercury deposition. *Environ. Research Sect. A*, 78, 118-133.

Bernatchez, P., 2003. Évolution littorale Holocène et actuelle des complexes deltaïques de Betsiamites et Manicouagan-Outarde : synthèse, processus, causes et perspectives. Ph. D. Thesis, Université Laval, 459 pp.

Bindler, R., 2006. Mired in the past — looking to the future: Geochemistry of peat and the analysis of past environmental changes. *Glob. Planet. Change*, 53, 209-221.

Bindler, R., Renberg, I., and Klaminder, J., 2008. Bridging the gap between ancient metal pollution and contemporary biogeochemistry. *J. Paleolimno.*, 40, 755-770.

Blaauw, M., 2010. Methods and codes for 'classical' age-modelling of radiocarbon sequences. *Quat. Geochron*., 5, 512-518.

Blais, J., 1996. Using isotopic tracers in lake sediments to assess atmospheric transport of lead in eastern Canada. *Water, Air, & Soil Poll.*, 92, 329-342.

Bollhöfer, A., and Rosman, K.J.R., 2002. The temporal stability in lead isotopic signatures at selected sites in the Southern and Northern Hemispheres. *Geochim. Cosmochim. Acta*, 66, 1375–1386.

Boutron, C.F., Gorlach, U., Candelone, J.-P., Bolshov, M.A., and Delmas, R.J., 1991. Decrease in anthropogenic lead, cadmium and zinc in Greenland snows since the late 1960s. *Nature*, 353, 153-156.

Boutron, C.F., Candelone, J.-P., and Hong, S., 1995. Greenland snow and ice cores: unique archives of large-scale pollution of the troposphere of the Northern Hemisphere by lead and other heavy metals. *Sci. Total Environ.*, 160/161, 233-241.

Boutron, C.F., 1995. Historical reconstruction of the earth's past atmospheric environment from Greenland and Antartic snow and ice cores. *Environ. Rev.*, 3, 1-28.

Brännvall, M.L., Bindler, R., Emteryd, O., Nilsson, M., and Renberg, I., 1997. Stable isotope and concentration records of atmospheric lead pollution in peat and lake sediments in Sweden. *Water, Air, & Soil Poll.,* 100, 243-252.

Brown, J.S., 1962. Ore leads and isotopes. *Econ. Geol.*, 57, 673-720.

Carignan, J., and Gariépy, C., 1995. Isotopic composition of epiphytic lichens as a tracer of the sources of atmospheric lead emissions in southern Québec, Canada. *Geochim. Cosmochim. Acta,* 59, 4427-4433.

Carignan, J., Simonetti, A., and Gariépy, C., 2002. Dispersal of atmospheric lead in northeastern North America as recorded by epiphytic lichens. *Atmos. Environ.*, 36, 3759-3766.

Couture, R.-M., Gobeil, C., and Tessier, A., 2008. Chronology of atmospheric deposition of arsenic inferred from reconstructed sedimentary records. *Environ. Sci. Technol.,* 42, 6508-6513.

Couture, R.-M., Gobeil, C., and Tessier, A., 2010. Arsenic, iron and and sulfur co-diagenesis in lake sediments. *Geochim. Cosmochim. Acta*, 74, 1238-1255.

Damman, A.W.H., 1986. Hydrology, development, and biogeochemistry of ombrogenous peat bogs with special reference to nutrient relocation in a western Newfoundland bog. *Can. J. Bot.,* 64, 384-394.

Davis, R.B., Hess, C.T., Norton, S.A., Hanson, D.W., Hoagland, and K.H., Anderson, D.S., 1984. ^{137}Cs and ^{210}Pb dating of sediments from softwater lakes in New England (U.S.A.) and Scandinavia, a failure of ^{137}Cs dating. *Chem. Geol.,* 44, 151–172.

Environment Canada, 2011. Canadian climate normal or averages 1971-2000. Environment Canada, Toronto, Ont. Online at: www.climate.weatheroffice.gc.ca/climate_normals/index_e.html

Evans, G.C., Norton, S.A., Fernandez, I.J., Kahl, J.S., and Hanson, D., 2005. Changes in concentrations of major elements and trace metals in Northeastern U.S.-Canadian sub-alpine forest floors. *Water, Air, & Soil Poll.,* 163, 245-267.

Frenette, P., (1996). *Histoire de la Côte-Nord*. Sainte-Foy, PUL (coll. « Les regions du Québec », no. 9), 667p.

Gallon, C., Tessier, A., Gobeil, C., and Beaudin, L., 2005. Sources and chronology of atmospheric lead deposition to a Canadian Shield lake: inference from Pb isotopes and PAH profiles. *Geochim. Cosmochim. Acta*, 69(13), 3199-3210.

Gallon, C., Tessier, A., and Gobeil, C., 2006. Historical perspective of industrial lead emissions to the atmosphere from a Canadian smelter. *Environ. Sci. Technol.*, 40, 741-747.

Gélinas, Y., Lucotte, M., and Schmit, J.P., 2000. History of the atmospheric deposition of major and trace elements in the industrialized St. Lawrence Valley, Quebec, Canada. *Atmos. Environ.,* 34, 1797-1810.

Givelet, N., Roos-Barraclough, F., and Shotyk, W., 2003. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural "background" values (past 8000 years). *J. Environ. Monit.,* 5, 935-949.

Goodfellow, W.D., 2002. Current understanding of the the origin of massive sulfide deposits in the Bathurst mining camp, Northern New Brunswick. *Gangue*, 72, 1-10.

Graney, J.R, Halliday, A.N., Keeler, G.J., Nriagu, J.O., Robbins, J.A., and Norton, S.A., 1995. Isotopic record of lead pollution in lead sediments from the northeastern United States. *Geochim. Cosmochim. Acta*, 59(9), 1715-1728.

Hamilton, T.F., and Smith, J.D., 1986. Improved alpha energy resolution for the determination of polonium isotopes by alpha-spectrometry. *Appl. Radiat. Isot.*, 37, 628–630.

Heiri, O., Lotter, A.F. and Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: Reproducibility and comparability of results. *J. Paleolimno*., 25(1), 101–110.

Hobson, G.D., 1969. Bedrock features of the Mer Bleue area by seismic methods. *Can. Field Nat.*, 84: 35–38.

Jeglum, J.K., Rothwell, R.L., Berry, and Smith, G.K.M. 1991. New volumetric sampler increases speed and accuracy of peat surveys. Tech. Note No. 9 Frontline Forestry Research Applications, Forestry Canada, Ontario Region, Sault Ste. Marie. 4 pp.

Joyal, R., (1970). Description de la tourbière à Sphaignes Mer Bleue près d’Ottawa. 1. Végétation. *Can. J. Bot.*, 48, 1405–1418.

Kada, J., and Heit, M., 1992. The inventories of anthropogenic Pb, Zn, As, Cd, and the radionnuclides 137Cs and excess 210Pb in lake sediments of the Adirondack region, USA. *Hydrobiologia*, 246, 231-241.

Komárek, M., Ettler, V., Chrastny, V. and Mihaljevic, M., 2008. Lead isotopes in environmental sciences: a review. *Environ. Intern.*, 34, no. 4, 562–577.

Krachler, M., Zheng, J., Fisher, D., and Shotyk, W., 2009. Global atmospheric As and Bi contamination preserved in 3000 year old Arctic ice. *Glob. Biogeochem. Cycles*, 23, 1-7.

Kylander, M.E., Weiss, D.J., and Kober, B., 2009. Two high resolution terrestrial records of atmospheric Pb deposition from New Brunswick, Canada, and Loch Laxford, Scotland. *Sci.Tot. Environ.*, 407, 1644-1657.

Laverdière, C., Bertrand, J. and Guimont, P., 1972**.** La carte géomorphologique; notes explicatives. Écologie de la Zone de l'Aéroport international de Montréal (EZAIM), Rapport préliminaire no II, Centre de recherches écologiques de Montréal, Montréal, 144 pp.

Le Roux, G., and De Vleeschouwer, F., 2010. Preparation of peat samples for inorganic geochemistry used as palaeoenvironmental proxies. *Mires and Peat, 7*, 1-9.

Livett, E. A., Lee, J. A., and Tallis, J. H., 1979. Lead, zinc and copper analyses of British blanket peats. *J. Ecol.*, 67, 865-891.

Lucotte, M., Mucci, A., Hillaire-Marcel, C., Pichet, P., and Grondin, A., 1995. Anthropogenic mercury enrichment in remote lakes of northern Québec (Canada). *Water, Air, & Soil Poll.*, 80, 467-476.

Manhès, G., Minster, J.F., and Allègre, C.J., 1978. Comparative uranium–thorium–lead and rubidium–strontium study of the Saint Sèverin amphoterite: consequences for early solar system chronology, *Earth Planet. Sci. Lett.,* 39, 14–24.

Mauquoy, D., van Geel, B., Blaauw, M., Speranza, A., and van der Plicht, J., 2004. Changes in solar activity and Holocene climatic shifts derived from ^{14}C wiggle-match dated peat deposits. *Holocene*, 14, 45–52.

Moore, T.R., Bubier, J.L., Frolking, S.E., Lafleur, P.M., and Roulet, N.T., 2002. Plant biomass and production and CO_2 exchange in an ombrotrophic bog. *J. Ecology*, 90, 25-36.

Muller, S., Richard, P.J.H., and Larouche, A.C., 2003. Holocene development of a peatland (southern Quebec): a spacio-temporal reconstruction based on pachymetry, sedimentology, microfossils and macrofossils. *Holocene*, 13, 649-644.

Nilsson, M., Klarqvist, M., Bohlin, E., and Possnert, G., 2001. Variation in ^{14}C age of macrofossils and different fractions of minute peat samples dated by AMS. *Holocene*, 11(5), 579–586.

Norton, S.A., Evans, G.C., and Kahl, J.S., 1997. Comparison of Hg and Pb fluxes to hummocks and hollows of ombrotrophic Big Heath Bog and to Nearby Sargent Mt. Pond, Maine, USA. *Water, Air, & Soil Poll.*, 100, 271-286.

Norton, S.A., Wilson, T., Handley, M., and Osterberg, E.C., 2007. Atmospheric deposition of cadmium in the northeastern USA. *Applied Geochem.*, 22, 1217-1222.

Nriagu, J.O., and Pacyna, J.M., 1988. Quantitative assessment of worlwide contamination of air, water and soils by trace metals. *Nature*, 333, 1343-1139.

Ouellet, M., and Jones, H.G., 1983. Paleolimnological evidence for the long-range atmospheric transport of acidic pollutants and heavy metals into the Province of Quebec, eastern Canada. *Can. J. Earth Sci*., 20, 23-36.

Outridge, P.M., Hermanson, M.H., and Lockhart, W.L., 2002. Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Arctic. *Geochim. Cosmochim. Acta*, 66(20), 3521-3531.

Poirier, A., Doucelance, R., and Gariépy, C., 2004. Radiogenic isotope investigation of the St-Robert H5 fall. *Meteorit. Planet. Sci.,* 39, 1983–1993.

Rabinowitz, M.B., and Wetherill, G.W., 1972. Identifying sources of lead contamination by stable isotope techniques. *Environ. Sci. Technol.*, 6, 705-709.

Rausch, N., Nieminen, T.M., Ukonmaanaho, L., Le Roux, G., Krachler, M., Cheburkin, A., Bonani, G., and Shotyk, W., 2005. Comparison of atmospheric deposition of copper, nickel, cobalt, zinc, and cadmium recorded by Finnish peat cores with monitoring data and emission records. *Environ. Sci. Technol.*, 39, 5989–5998.

Reimer, P.J., Baillie, M.G.L., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Bronk Ramsey, C., Buck, C.E., Burr, G.S., Edwards, R.L., Friedrich, M., Grrotes, P.M., Guilderson, T.P., Hajdas, I., Heaton, T.J., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B., McCormac, F.G., Manning, S.W., Reimer, R.W., Richards, D.A., Southon, J.R., Talamo, S., Turney, C.S.M., van der Plicht, J. and Weyhenmeyer, C.E., 2009. IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal BP. *Radiocarbon*, 51, 1111-1150.

Roos-Barraclough, F., Givelet, N., Cheburkin, A.K., Shotyk, W., and Norton, S.A., 2006. Use of Br and Se in Peat To Reconstruct the Natural and Anthropogenic Fluxes of Atmospheric Hg: A 10000-Year Record from Caribou Bog, Maine. *Environ. Sci. Technol.*, 40, 3188-3194.

Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone, J.P., and Hong, S., 1994. Isotopic evidence to account for changes in the concentration of in Greenland snow between 1960 and 1988. *Geochim. Cosmochim. Acta*, 58(15), 3265-3269.

Roulet, N., Lafleur, P., Richard, P., Moore, T., Humphreys, E., and Bubier, J., 2007. Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland. *Glob. Change Biol.*, 13, 397–411.

Shotyk, W., 1988. Review of the inorganic geochemistry of peats and peatland waters. *Earth Sci. Rev.*, 25, 95-176.

Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A., and Kramers, J.D., 1996. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. *Earth Planet. Sci. Lett.*, 145, E1-E7.

Shotyk, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., and Van Der Knaap, W.O., 1998. History of atmospheric lead deposition Since 12,370 14C yr BP from a peat bog, Jura Mountains, Switzerland. *Science*, 281, 1635-1640.

Shotyk, W., Weiss, D., Kramers, J.D., Frei, R., Cheburkin, A.K., Gloor, M., and Reese, R., 2001. Geochemistry of the peat bog at Étang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr and REE) since 12,370 ^{14}C yr BP. *Geochim. Cosmochim. Acta*, 65, 2337-2360.

Shotyk, W., Weiss, D., Heisterkamp, M., Cheburkin, A.K., Appleby, P.G., and Adams, F.C., 2002. New peat bog record of atmospheric lead pollution in Switzerland: Pb concentrations, enrichment factors, isotopic composition, and organolead species. *Environ. Sci. Technol.*, 36, 3893-3900.

Shotyk, W., and Krachler, M., 2010. The isotopic evolution of atmospheric Pb in central Ontario since AD 1800, and its impacts on the soils, waters, and sediments of a forested watershed, Kawagama Lake. *Geochim. Cosmochim. Acta*, 74, 1963-1981.

Simonetti, A., Gariépy, C., and Carignan, J., 2000. Pb and Sr isotpic evidence for sources of atmospheric heavy metals and their deposition budgets in northeastern North America. *Geochim. Cosmochim. Acta*, 64, 3439-3452.

Simonetti, A., Gariepy, C., Banic, C. M., Tanabe, R., and Wong, H. K., 2004. Pb isotopic investigation of aircraft-sampled emissions from the Horne smelter (Rouyn, Québec): Implications for atmospheric pollution in northeastern North America. *Geochim. Cosmochim. Acta*, 68, 3285-3294.

Sturges, W.T., and Barrie, L.A., 1987. Lead 206/207 isotope ratios in the atmosphere of North America as tracers of US and Canadian emissions. *Nature*, 329, 144-146.

Sturges, W.T., and Barrie, L.A., 1989. The use of stable lead 206/207 isotope ratios and elemental composition to discriminate the origins of lead in aerosols at a rural site in Eastern Canada. *Atmos. Environ.*, 28, 1645-1657.

Taylor, R.E., 1997. Radiocarbon dating. In Taylor, R.E.and Aitken, M.J. (eds), *Chronometric Dating in Archeology*; pp.65-96. New York: Plenum Press. *Advances in Archeological Museum of Science 2*.

Taylor, S.R., and McLennan, S.M., 1995. The geochemical evolution of the continental crust. *Rev. Geophys.*, 33, 241-265.

Tessier, A., Gobeil, C., and Couture, R-M., 2012. Stable Pb isotope ratios as mid-1800s stratigraphic markers for sediments from Eastern Canada lakes. 22nd Goldschmidt, Montreal.

Wedepohl, K.H., 1995. The composition of the continental crust. *Geochim. Cosmoschim. Acta*, 59, 1217-1232.

U.S. Energy Information Administration, Annual Energy Review, 2009, pp. 408 (released Aug. 2010).

Vile, M.A., Wieder, R.K., and Novak, M., 1999. Mobility of Pb in Sphagnum-derived peat. *Biogeochemistry*, 45, 35-52.

Weiss, D., Shotyk, W., and Kempf, O., 1999a. Archives of atmospheric lead pollution. *Naturwissenschaften*, 86, 262-275.

Weiss, D., Shotyk, W., Appleby, G., Kramers, J.D., and Cheburkin, A.K., 1999b. Atmospheric Pb deposition since the Industrial Revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environ. Sci. Technol.*, 33, 1340-1352.

Weiss, D., Shotyk, W., Boyle, E.A., Kramers, J.D., Appleby, P.G., and Cheburkin, A.K., 2002. Comparative study of the temporal evolution of atmospheric lead deposition in Scotland and eastern Canada using blanket peat bogs. *Sci. Tot. Environ.*, 292, 7-18.

Chapter 3: Final remarks

3.1 Research summary and conclusions

Human activities, especially since the Industrial Revolution (1820-1870AD), significantly modified the geochemical cycles of several elements, with adverse effects on ecosystems and human health (Nriagu and Pacyna, 1988). This large-scale contamination has been recorded in a variety of archives such as lacustrine and marine sediments, ice cores and peat bogs. Ombrotrophic peatlands (peat bogs) are increasingly recognized as effective archives of atmospheric trace metal deposition (Weiss *et al.*, 1999; Bindler, 2006). Being an important natural wind corridor, oriented from south-west to north-east, the St. Lawrence Valley is affected by long-range transport of contaminants originating from urban and industrialized areas in western Quebec, eastern Ontario and the U.S. Mid-West (Fig. 2.1; Chapter 2). With this in mind, the main objective of this project was to reconstruct the history of atmospheric trace metal deposition along the St. Lawrence Valley using peat bog cores.

Surface cores (< 100 cm long) were retrieved from three ombrotrophic peatlands on a south-west to north-east transect along the St. Lawrence Valley. The As, Cd, Ni, Pb and Zn concentrations, as well as the stable Pb isotope composition, were measured on the sectioned cores. Both ^{210}Pb analyses and radiocarbon dating of the core sections were used to build age-depth models for each of the peat profiles. In turn, the As, Cd, Ni, Pb and Zn accumulation rates and their variation in time were computed. Stable Pb isotopes were analysed to discriminate between natural and anthropogenic sources of Pb, including apportioning the Pb originating from Canadian and U.S. gasoline additives between 1960 and 1976.

The similarity of the As, Cd and, to a certain extent, Ni and Zn, accumulation rate patterns with those of Pb in the Mirabel and Mer Bleue cores suggests that these elements are effectively retained in the peat column and, thus, provide a reliable historical record of their atmospheric deposition. In contrast, the Ni record in the Baie peatland seems to have been affected by post-depositional remobilization.

Likewise, Zn was enriched at the surface of the Baie and Mirabel cores through bioaccumulation by living vegetation.

The trace metal accumulation rates and stable Pb isotope signatures show that the onset of important metal deposition started around 1810-1850 AD in the three bogs. The As, Cd, Ni and Pb accumulation rate records for the two southwestern cores (Mirabel and Mer Bleue) are chronologically very similar, *i.e.* they show similar patterns and two peaks dated at 1940's and late 1960's to early 1970's. On the other hand, the chronology of Pb accumulation in the Baie core differs from the two other sites with a single peak spanning between 1951 and 1961AD. The discrepancy is probably attributable to the lower peat accumulation rate and temporal resolution of the core. Nevertheless, the source of atmospheric Pb in the Baie core is likely the same as the two other cores, i.e. coal burning and ore smelting until the 1950's and leaded gasolines until their phase-out in 1976. The As and Cd accumulation rates in the Baie core are too low to discern a temporal pattern, while the Ni and Zn records show, respectively, signs of post-depositional remobilization and partial bioaccumulation by surface vegetation.

The stable Pb isotope records suggest that coal burning, ore smelting and metal refining were the main sources of trace metals during the 19th century and early 20th century. From the 1940's, ^{206}Pb:^{207}Pb ratios were nearly constant in the Mer Bleue and Baie cores, with values of 1.178 and 1.165 respectively, and increased slightly after the mid-1960's and early-1970's, suggesting that the main Pb source became the combustion of leaded gasolines until the 1976.

The Mer Bleue and Mirabel peatland cores show greater metal deposition rates (2 to 10 times greater depending on the metal) than at the Baie peatland, located around 600 km to the north-east. Likewise, stable Pb isotope apportionment calculations, for the period between 1960 and 1980, reveal that the south-western part of the St. Lawrence Valley (Mer Bleue peatland) received more lead originating from U.S. (55%) than Canadian gasoline additives further to the north-east (Baie peatland; 35%). The greater accumulation rates and more radiogenic Pb isotope signatures found in the southern part of the Valley likely reflect their greater proximity to contaminant sources (Carignan *et al.*, 2002; Lucotte *et al.*, 1995) and their progressive washout as air masses travel from the Great Lakes/American Mid-west region to the Gulf of St. Lawrence. This highlights the importance of trans-boundary transport of atmospheric metals from the Eastern and U.S. Mid-West to southern Quebec and more specifically along the St. Lawrence Valley.

The sharp decrease in metal accumulation rates since the late 1960's and early 1970's show that mitigation policies implemented at the beginning of the 1970's have been effective in reducing atmospheric trace metal emissions. Nevertheless, the current metal accumulation rates are still one order of magnitude higher than pre-industrial values. Likewise, despite the phasing-out of leaded gasolines and better control on trace metal emissions, the stable Pb isotopic ratios recorded in the 1980's have not reverted back their pre-industrial values. This can be explained by the emergence of other industrial sources, such as ore smelting and refining or coal burning.

3.2 Final recommendations

Some compression occurred during the collection of two of the three cores. Core compression could reduce the temporal resolution of anthropogenic metal deposition by affecting the activity of ^{210}Pb and trace metal concentrations obtained as peat layers will encompass more years than they would normally. To lessen the risk of compression, a Waardenar corer should be used, it is specifically designed to avoid compression of porous samples (Givelet *et al.*, 2004).

The cores were sliced fresh using a serrated, ceramic knife, which carry the risk of incorporating material from adjacent samples, especially for sections dominated by loose material, like the core surface and/or sections containing roots. These portions of the core are more subject to lateral compression and are often those recording the anthropogenic impacts. This sampling protocol could alter the intensity of trace metal peaks and their chronology as each slice represents an average over a set period of time and the incorporation of 'foreign' material or compression would modify this average. It is thus important to be careful as the reliability of the reconstructed records partly lies in the precision of the cutting process and density measurements of the samples. The core slicing method could be improved by 1) freezing the core and 2) using a band-saw (Givelet *et al.*, 2004). This would allow more control on the thickness of the sections and precise measurements of the bulk density and, hence, better estimates of the accumulation rates and age models (^{210}Pb) as density is used in their calculation.

As observed in the Mer Bleue core, fires can alter peat profiles and greatly complicate the estimation of historical accumulation rates. A peatland fire would burn part of the accumulated material and some crucial information would be lost. Whenever possible, profiles disrupted by fire or other processes should be avoided as they may not be reliable archives of trace metal deposition.

Complete peat profiles (i.e. down to the bottom sediments or bedrock) should be analyzed to better constrain the natural variability in the Pb isotopic composition. Anthropogenic contamination by As, Pb, Zn and other chalcophile elements extending back 3000 years were reported in an ice core from Devon Island in the Canadian Arctic (Zheng *et al.*, 2007; Krachler *et al.*, 2009). Consequently, whenever available, the oldest ombrotrophic peat sections should be analysed to ensure that the natural trace metal concentrations, accumulation rates, and stable Pb isotopic ratios are properly determined.

Cores from other peat bogs along the St. Lawrence Valley should be collected and analysed to verify if the pattern found in the south-western part of the valley is recorded elsewhere. Furthermore, this would allow a better reconstruction of the gradient in trace metal deposition and stable Pb isotope ratios along the St. Lawrence Valley. Although it has been partly done using lacustrine sediments and epiphytic lichens (Carignan *et al.*, 2002; Lucotte et al., 1995; Gallon *et al.*, 2005), peat bogs usually provide a greater time resolution and a more reliable record than lake sediments since the latter require a consideration of diagenetic remobilization (i.e., application of diagenetic models to reconstruct the original depositional record), and lichens integrate atmospheric deposition over their life span (several decades). Peat cores collected from other geographical and climatic regions could provide an independent evaluation of the geochemical behaviour and fate of trace metals, other than Pb, and help confirm the hypothesis that their original depositional record is preserved in the peat column. To further confirm this hypothesis or to determine the rate of post-depositional remobilization in these environments, pore water metal concentration profiles should be determined. Comparison of pore water concentrations with those in solid peat (Rausch *et al.*, 2005) or pore water vertical gradients (Novak and Pacherova, 2008) can be used to evaluate if and how fast trace metals are remobilized. This could be further addressed by comparing trace metal accumulation rates and pore water concentrations derived from peat bog cores recovered at locations where historical records of point-source anthropogenic emissions are well documented, such as in the vicinity of the Noranda smelter in northwestern Quebec.

3.3 References

Bindler, R., 2006. Mired in past – looking to the future: geochemistry of peat and the analysis of past environmental changes. *Glob. Planet. Change*, 53, 209-221.

Carignan, J., Simonetti , A., and Gariépy, C., 2002. Dispersal of atmospheric lead in northeastern North America as recorded by epiphytic lichens. *Atmos. Environ.*, 36, 3759-3766.

Gallon, C., Tessier, A., Gobeil, C., and Beaudin, L., 2005. Sources and chronology of atmospheric lead deposition to a Canadian Shield lake: inference from Pb isotopes and PAH profiles. *Geochim. Cosmochim. Acta*, 69(13), 3199-3210.

Givelet, N., Le Roux, G., Cheburkin, A., Chen, B., Frank, J., Goodsite, M.E., Kempter, H., Krachler, M., Noernberg, T., Rausch, N., Rheinberger, S., Roos-Barraclough, F., Saptoka, A., Scolz, C., and Shotyk, W., 2004. Suggested protocol for collecting, handling and preparing peat cores and samples, for physical, chemical, mineralogical and isotopic analyses. *J. Environ. Monit.*, 6, 481-492.

Krachler, M., Zheng, J., Fisher, D., and Shotyk, W., 2009. Global atmospheric As and Bi contamination preserved in 3000 year old Arctic ice. *Glob. Biogeochem. Cycles*, 23, GB3011.

Lucotte, M., Mucci, A., Hillaire-Marcel, C., Pichet, P., and Grondin, A., 1995. Anthropogenic mercury enrichment in remote lakes of Northern Québec (Canada). *Water, Air and Soil Poll.*, 80, 467-476.

Novak, M., and Pacherova, P., 2008. Mobility of trace metals in pore waters of two Central European peat bogs. *Sci. Total Environ.*, 394, 331-337.

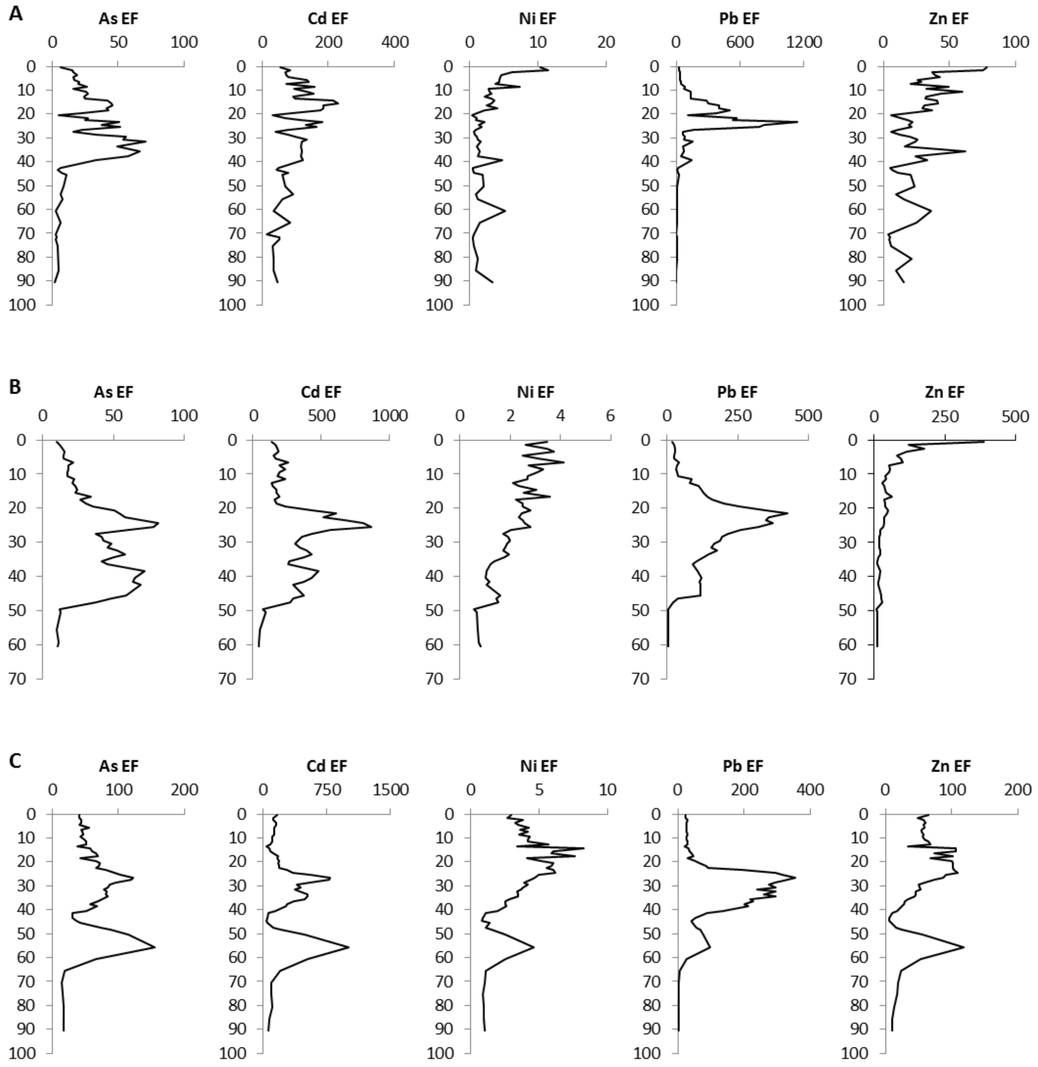
Nriagu, J.O., and Pacyna, J.M., 1988. Quantitative assessment of of worldwide contamination of of air water and soils by trace metals. *Nature*, 333, 134-139.

Weiss, D., Shotyk, W., Appleby, G., Kramers, J.D., and Cheburkin, A. K., 1999. Atmospheric Pb deposition since the Industrial Revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environ. Sci. Technol.*, 33, 1340-1352.

Raush, N., Ukonmaanaho, L., Nieminen, T.M., Krachler, M., and Shotyk, W., 2005. Porewater evidence of metal (Cu, Ni, Co, Zn, Cd) mobilization in an acidic, ombrotrophic bog, impacted by a smelter, Harjavalta, Finland and comparison with reference sites. *Environ. Sci. Technol.*, 39, 8207-8213.

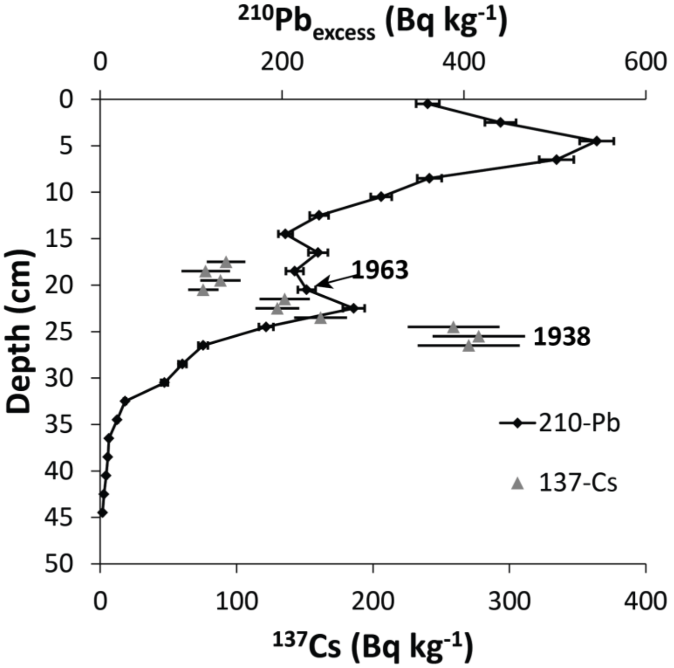
Zheng, J., Shotyk, W., Krachler, M., and Fisher, D.A., 2007. A 15,800-year record of atmospheric lead deposition on the Devon Island Ice Cap, Nunavut, Canada: natural and anthropogenic enrichments, isotopic composition, and predominant sources. *Glob. Biogeochem. Cycles*, 21, GB2027.

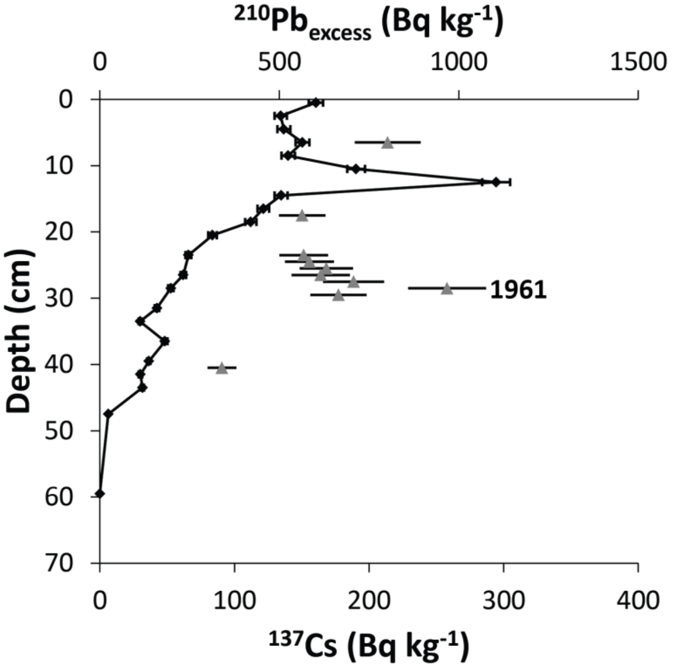
Appendix 1: Metal enrichment factors



Appendix 1.1: Metal enrichment factor profiles calculated from Sc for the Baie (A), Mirabel (B) and Mer Bleue (C) cores.

Appendix 2: ^{137}Cs results





Appendix 2.1: ^{137}Cs and ^{210}Pb activities profiles for the Baie (A) and Mirabel (B) cores.